BIRMINGHAM FREE LIBRARIES.

REFERENCE DEPARTMENT. No. 247251

The Figures below state the Dates on which this Book has been issued.

Added Dec 1913

Issues		
8.12.13	29.6.15	8-5-17
16-12-13	2-7-15	31.5.17
11.2.14	8-10-15	14-11-16
18.2.14	8.1.16	16.2.17
8.7.14	17-1-16	16.XI.50.
11.7.14	4.7.16	
19.9.14	2.3.16	
21.8.14	20.3.16	
2.9.14	22.4.16	
15.9.14	26.4.16	
18.1.15	11.5.16	
10.3.15	5.6.16	
4.4.15	6.6.16	
19.4.15	7.6.16	
6.5.15	5-1-17	
19.6.15	V.1.17.	
	8.V.17.	

X668.7

Title and Author	Coal-Tar and Ammonia, by G. Lunge. Part. 1. 1909.
Number	547251 A — Date of Acquisition Dec. 1913
Collation	Pp. XX, 564. Errata slip facing p. XX. 1.12.13 L.W.P.
Catalogue Entries	Lunge: Coal-Tar: Ammonia: Chemistry (Other Trades)
Catalogue References	Tar: see Coal-Tar:
Date of Re-binding, &c.	Catalogued by - KW. Checked by - HMG
Stamped by	J.H. — Cut by
Record of Issues	..... Issues from ..... to .... " " ..... " .... " " ..... " .... " " ..... " .... " " ..... " .....

(B8358)

COAL-TAR AND AMMONIA

PART I

WORKS BY GEORGE LUNGE, Ph.D., Dr.Ing.

Technical Methods of Chemical Analysis. *English Translation by* CHAS. ALEX. KEANE, D.Sc., Ph.D.

Vol. I., in Two Parts, royal 8vo, 1024 pp., *not sold separately. Recently published.* Price £2, 12s. 6d. *net.*

Vols. II. and III. (each Volume sold separately). *In active preparation.*

Technical Chemists' Handbook. Tables and Methods of Analysis for Manufacturers of Inorganic Chemical Products, being a thoroughly revised and extended edition of *Alkali Makers' Handbook*, indispensable for the Technical Chemist. *Recently published*, crown 8vo, 280 pp., bound in leather. Price 10s. 6d. *net.*

The Manufacture of Sulphuric Acid and Alkali. A Theoretical and Practical Treatise.

Vol. I.—Sulphuric Acid, in Two Parts, 1200 pp., *not sold separately.* Third and much enlarged Edition. Price £2, 12s. 6d.

Vol. II.—Salt Cake, Hydrochloric Acid, and Leblanc Soda, 1050 pp. Third and much enlarged Edition. *In Two Parts, not sold separately.* Price £2, 2s.

Vol. III.—The Ammonia-Soda and various other Processes of Alkali-Making, 800 pp. Second Edition, Revised and Enlarged. Price £2, 2s.

Coal-Tar and Ammonia. Fourth and much Enlarged Edition, 1200 pp. *In Two Parts, not sold separately.* Price £2, 2s. *net.*

Handbook of Technical Gas-Analysis. By CLEMENS WINKLER, Ph.D. Translated by Professor LUNGE. Second English Edition. Price 10s. 6d.

LONDON: GURNEY & JACKSON, 10 PATERNOSTER ROW

COAL-TAR AND AMMONIA

BY GEORGE LUNGE, PH.D.

PROFESSOR EMERITUS OF TECHNICAL CHEMISTRY IN THE FEDERAL POLYTECHNICUM, ZURICH

HONORARY AND FOREIGN MEMBER OF THE CHEMICAL SOCIETY, LONDON, AND OF THE AMERICAN CHEMICAL SOCIETY

DR.ING. (H.C.) OF KARLSRUHE, ETC., ETC.

FOURTH AND ENLARGED EDITION

PART I

GURNEY AND JACKSON

10 PATERNOSTER ROW, LONDON, E.C.

1909

BIRMINGHAM REFERENCE LIBRARY PUBLIC LIBRARIES

247/251A

PREFACE TO THE FOURTH EDITION

THE last edition of this treatise appeared in 1900. I had for that edition enjoyed the co-operation of Dr H. Köhler—a gentleman actively employed in the industry of tar-distilling and already known in the literary field. A new issue having become necessary, the text of the last edition was thoroughly overhauled and completed by the vast amount of fresh matter accumulated in the interval. For the major part of this new edition—viz., all the chapters dealing with Coal-tar and the products made therefrom (Chapters I. to XI.)—I have this time been favoured with the services of one of the greatest authorities in that domain, Dr G. Kraemer of Berlin, who has had the great kindness to look over the proofs and to give me the benefit of corrections and additions taken from his vast experience.

I therefore indulge in the hope that this fourth edition will meet with the same favourable reception as its predecessors, and will prove of use to all interested in the industries described here.

THE AUTHOR.

ZURICH, *November* 1909.

CONTENTS

PREFACE v

PART I

CHAPTER I

INTRODUCTORY

	PAGE
Object of destructive distillation	1
Solid residue	1
Permanent gases	2
Watery distillates	2
Tars	3
from browncoal, peat, and shale	3
Coal-tar	4
Theory of the formation of tar	4
Chemical structure of coal	4
Formation of tar	5
Historical Notes on the application of coal-tar and the products obtained therefrom	6
Origin of tar-distilling	9
Impetus given to this by the discovery of aniline colours	9
Present state	10
Quantity of coal-tar produced	11
Statistics up to 1897	12
Statistics for the last ten years	13

CHAPTER II

PROCESSES FOR OBTAINING COAL-TAR

A. THE PRODUCTION OF COAL-TAR AT THE GAS-WORKS	18
Condensation of tar	18
Influence of the temperature of destructive distillation on the tar	19
Differences among tars from various raw materials	19
And at high or low temperatures	21
Influence of the shape of the retorts (horizontal, vertical)	24
of the variations of pressure (exhausters)	24
of the quality of the coal	25
Tar from Boghead or cannel coals	25
Yield of tar from coal	28
Proposals for increasing the quantity or improving the quality of tar in the manufacture of coal-gas	30
Recovery of the tar suspended in the gas	32
Process of Pelouze and Audouin	33
A. THE PRODUCTION OF COAL-TAR AT THE GAS-WORKS—*contd.*	
Other apparatus for removing the tar	36
Recovery of benzol contained as vapour in coal-gas	36
Quantity of benzol in coal-gas	37
Recovery by pressure	38
by cooling	40
by liquid absorbents	40
from coke-oven gases	43
Process of Carvès	43
of Hirzel	45
Other processes for extracting the benzol from gases	50
Recovering the benzol from gases as nitrobenzol	52
Composition of benzol obtained from coal-gas	53
Estimation of benzol contained in gases	55

PAGE

B. TAR (AND AMMONIA) OBTAINED AS BY-PRODUCT IN COKE-MAKING 57
First attempts 57
Knab's oven 58
Carvès' oven 60
Other ovens 60
Enumeration of patents . . 62
Special descriptions :—
1. *Modified Beehive Ovens* . . 65
Jameson's oven . . . 66
Other ovens of this class . 67
2. *Recovery Ovens on the modified Coppée System* . . . 70
Lürmann's oven . . . 70
Hoffmann-Otto ovens . . 71
Otto-Hilgenstock ovens . . 78
Similar ovens 81
3. *Recovery Ovens on the modified Carvès System* . . . 85
Carvès new oven (Simon-Carvès oven) . . . 86
Hüssener's oven . . . 93
Semet-Solvay ovens . . 97
Other ovens 102
Recent patents . . . 103
Condensing plant for tar and ammonia from coke-ovens . . 104
For Otto ovens 104
Description by Henss . . . 107
Quality of the tar produced in various forms of coke-ovens . 111
tar from Jameson's ovens . . 111
from Simon-Carvès ovens . . 112
from Otto-Hoffmann ovens . 114
from "Hibernia" ovens . . 114
from Semet-Solvay ovens . . 116
Comparison of yields of products from coke-oven tar and gas-tar 117
General conclusions . . . 117
Question of coking all coal now used for manufacturing purposes . 118

PAGE

B. TAR (AND AMMONIA) OBTAINED AS BY-PRODUCT IN COKE-MAKING—*continued.*
Recovery of ethylene from coke-oven gases 119
Illuminating gas from coke-ovens . 119
Statistics of the recovery of tar and ammonia from coke-oven tar . 123
Total production of coke . . 123
Tar and ammonia from coke-ovens in Germany 123
in the United Kingdom, etc. . 126
in the United States . . . 126
General remarks 127
C. TAR (AND AMMONIA) FROM GAS-PRODUCERS 128
D. TAR (AND AMMONIA) FROM BLAST-FURNACE GASES . . . 130
Gartsherrie process . . . 132
Other processes 133
State of matters in 1902 . . 135
Composition of blast-furnace tar . 136
Uses of this tar 138
E. TAR FROM WATER-GAS . . 139
F. TAR AND TAR-PRODUCTS OBTAINED BY SUPERHEATING CERTAIN OILS AND VAPOURS . 141
Production of tar in the manufacture of oil-gas 141
Properties and uses of oil-gas tar . 143
Tar obtained by superheating petroleum residues, etc. . . 144
G. SYNTHETIC PRODUCTION OF AROMATIC HYDROCARBONS BY MEANS OF BARIUM CARBIDE . 149
General observations on coal-tar from various sources . . 150
Determination of the yield of tar and ammonia from coal . . 152
General observations on the supply of coal-tar for industrial purposes 154

CHAPTER III

THE PROPERTIES OF COAL-TAR AND ITS CONSTITUENTS

General properties of coal-tar . . 159
Enumeration of the compounds found in coal-tar 160
Hydrocarbons of the methane series (paraffins) 165
Ethylene series (olefins) . . . 169

	PAGE
Aromatic addition-products	172
Acetylene series	173
Series C_nH_{2n-4}	174
Benzene series	176
Benzene	177
Toluene	183
Xylenes	184
Trimethylbenzenes	186
Ethylbenzene	187
Tetramethylbenzenes	188
Naphthenes	188
Styrolene	188
Indene	189
Methylindenes	190
Naphthalene	190
Naphthalene hydrides	192
Methylnaphthalenes	193
Phenylnaphthalenes	194
Acenapthene	194
Diphenyl	194
Fluorene	195
Anthracene	196
Hydrides of anthracene	199
Paranthracene	200
Methylanthracenes	200
Phenanthrene	201
Synanthrene	203
Fluoranthrene	203
Pyrene	203
Chrysene	204
Truxene	205
Chrysogen	205
Retene	206
Succisterene	206
Picene	206
Benzerythrene	207
Crackene	207
Bitumens	208
Oxygenized compounds	208
Alcohols	208
Acetone	209
Acetic acid	209
Benzoic acid	209
Phenol (carbolic acid)	209
Cresols	215
Xylenols	218
Naphthols	220
Anthrol, phenanthrol	220
Rosolic acid	220
Brunolic acid	222
Cumarone	222
Paracumarone	223
Methylcumarones	223
Naphthofuran	224
Diphenylene oxide	224
Sulphuretted compounds	225
Carbon bisulphide	225
Carbon oxysulphide	225
Thiophen	226
Methylthiophens	227
Diphenylene sulphide	227
Mercaptans	228
Free sulphur	228
Nitrogenized Compounds—A. Basic —Ammonia	228
Substituted ammonias	228
Cespitine	229
Aniline	229
Pyridine series	230
Pyridine	230
Picoline	232
Lutidines	232
Collidines, etc.	233
Parvolines	233
Coridines	234
Rubidine	234
Viridine	234
Quinoline series	234
Acridine	236
Other bases	237
B. Not basic—Pyrrol	237
Cyanogen compounds	238
Carbazol	239
Phenylnaphthyl-carbazol	240
Free carbon	240
Theory of the formation of the constituents of coal-tar	241
Appendix—Poisonous quality of coal-tar	246

CHAPTER IV

APPLICATIONS OF COAL-TAR WITHOUT DISTILLATION

	PAGE
Introductory	247
Employment of coal-tar for the manufacture of gas	248
Former processes	248
Dinsmore process	249
Use for enriching water-gas	251
Burning tar as fuel	251
First attempts	252
Descriptions of recent methods	252
Liegel's	253
Schilling's	254
Various patents	256
Burning by the "forsunka"	258
Lenz's burners	260
Brandt's	262
Kaufman's	264
Nobel's	265
Körting's spray-producer	267
Various processes	267
The relative calorific effects of coal-tar and coke for retort-firing	273
Papers by Dexter	273
by Lewis	273
by Wright	276
by Körting	276
by others	277
Heating coke-ovens	277
Employment of coal-tar for preserving timber, stone, iron, etc.	278
Employment of coal-tar for the manufacture of roofing-felt	280
Description of a modern plant	281
Recent patents	286
Coal-tar as a cementing substance	287
Coal-tar used for making and improving roads	288
Dörrite	290
Asphalt and pitch from tar without distilling it	291
Solidified tar	293
Coal-tar and preparations from it for antiseptic and medicinal purposes	293
Coal-tar for denaturing alcohol	295
The manufacture of lampblack and soot	295
Ordinary lampblack furnaces	296
Modern furnaces	298
Apparatus for catching the soot	300
Calcining the soot	302
Purification	302
Printers' ink	303
Recent patents	304
Applications of soot	305
Coke from tar	305

CHAPTER V

THE FIRST DISTILLATION OF COAL-TAR

Historical notes	306
Carriage and storage of coal-tar	308
Boats, tank-waggons	308
Barrels	310
Store tanks, wells	308
Pumping the tar	309
Distillation by steam	312
Quality of naphtha from this process	313
Distillation by fire	314
Dehydration of the tar	314
by application of heat	315
by means of quicklime or calcium sulphate, as applied to water-gas tar	320
Dehydration of the tar—*continued.* by centrifugals	320
in other ways	321
Previous purification from free carbon	321
Purification of blast-furnace tar from solid impurities	323
Construction of tar-stills	323
Material	323
Shape	325
Upright cylinders	325
Horizontal cylinders	327
Waggon-shaped stills	328
Detailed description of a 25-ton still	331
Mountings of the still	333
Setting tar-stills	340

	PAGE
Condensing apparatus	343
Receivers	348
To be used for pumping the oils by air-pressure	350
Treatment of the gases escaping from the condensers	351
Working of the tar-stills	335
Charging	335
Heating up and preventing the boiling-over	356
Separation of fractions	358
Ascertaining the specific gravities at higher temperatures	359
Enumeration of fractions	360
Nature of fractional distillation	362
First runnings	363
Light oil	364
Carbolic oil	366
Creosote oil	368
Anthracene oil	369
End of the distillation	369
Distilling to hard pitch in a separate still	371
Employment of steam in the last stage	372
Mechanical agitators in tar-stills	375
Distillation in a current of inert gases	377
Employment of a vacuum	378
Running off the pitch	383
Softening pitch in the retort	383
Hard pitch	384
Pitch-cooler	385
Pitch-bags	388
Continuous distillation of tar	392
Vohl's still	392
Lennard's still	394
Newest shape of his apparatus	396
Mason's still	398
Pfropfe's still	399
Hirzel's still	401
Köhn's apparatus	402
Ray's still	404
Wilson's still	405
Recent patents	405
Distillation of tar for the purpose of making illuminating gas	405
Other methods for distilling coal-tar	408
Results of work, yields, etc.	408
Testing of tar in the laboratory	418
Estimation of specific gravity	425
of free carbon	426
of water	427

CHAPTER VI

PITCH

	PAGE
Nature of coal-tar pitch	429
General properties; soft and hard pitch	430
Softening pitch in special apparatus	433
The manufacture of patent fuel (briquettes)	435
Testing the quality of briquettes	440
Varnishes with pitch	441
Refined ("prepared") tar	441
Testing its quality--method of Lunge	443
Better varnishes	445
Asphalt	446
Use for street-paving	447
Tar pavement	449
Mixtures with brimstone (wood-cement)	450
Asphalt pipes	451
Use for insulating cables, etc.	453
The distillation of pitch for coke	454
Brick pitch-ovens	454
Apparatus of Fenner and Vermann	457
Other methods of coking pitch	461
Quality of the coke	461
Other uses of coal-tar pitch	462
Testing of pitch	464
Softening- or melting-point	464
Viscosity	468
Percentage of real bitumen	469
Distinction between ordinary coal-tar pitch and blast-furnace pitch	470
from natural asphalt	470
from lignite tar	471
Statistics	472

CHAPTER VII

ANTHRACENE OIL

	PAGE
General properties	473
Crystallization by cooling	474
Filtering in bags	474
Filter-presses	476
Centrifugals	476
Hydraulic presses	477
Comparison of filtering methods	482
Special methods	480
Oils draining from rough anthracene	480
Extracting anthracene from these	481
Employment for printers' ink	483
For preserving timber (carbolineum)	483
For removing naphthalene from coal-gas	485
Purification of pressed anthracene oil by washing	486
with solvent naphtha	486
with petroleum-spirit	488
with creosote oil	489
with caustic potash	491
with paraffin oil or oleic acid	493
with pyridine bases	493
by sulphur dioxide	495
by acetone	495
by liquid ammonia	495
Various methods	495
Chemically pure anthracene	496
Subliming the anthracene	497
Anthracene obtained synthetically	498
Preparation of phenanthrene, fluorene, and carbazol, as by-products	499
Yields and statistics	501
Properties and analysis of anthracene	503
Substances contained in rough anthracene	503
General remarks on its analysis	503
Sampling	504
Alcohol test	504
Bisulphide of carbon test	506
Anthraquinone test	507
Luck's method	508
Objections to it	509
Höchst test	511
Table for calculating the results	512
Remarks upon this test	512
Modifications of it	513
Estimation of the paraffin contained in anthracene	514
Nickels' test	514
Estimation of anthracene present in tar	519
Analytical methods for carbazol	519
for phenanthrene	520

CHAPTER VIII

CREOSOTE OIL

Store tanks	522
Properties	523
Composition	523
Redistillation	525
Treatment for special purposes	526
Removing the smell	526
Disinfecting powder	527
Emulsions of creosote oil or its distillates (creoline, lysol, etc.)	527
Pitch from creosote oil	530
Mixtures with other substances	530
Uses of creosote oil	530
as fuel	530
as lubricant	531
for lighting	532
Creosote oil and preparations from it as antiseptics	538
Application for pickling timber	539
Historical	539
Apparatus for that purpose	540
Difficulty caused by moisture	542
Boulton's process	543
Other apparatus	544
Advantages of creosoting wood	546
Part played by naphthalene	548
Requirements concerning the quality of the oil	550
Report of Mr Boulton	551
of Dr Tidy	552
his specification as amended in 1885, with process for determining the coal-tar acids	554

PAGE

Application for pickling timber—*contd.*
Sir F. Abel's specification . . 555
Specification of the Prussian Railroad management . . . 557
Employing creosote oil together with zinc chloride . . . 558
Other additions to creosote oils . 558
Decomposition of heavy tar oils by heat (cracking) 558
Application of creosote oil for the "blue-steaming" of bricks . 562
Carriage of creosote oils . . . 563

PART II

CHAPTER IX

CARBOLIC ACID AND NAPHTHALENE

Carbolic acid (phenol) . . . 564
Fraction taken as carbolic oil . . 564
Redistillation 565
Separation of carbolic acid and cresols 567
Treatment with caustic alkali . 567
Fractional saturation . . . 568
Apparatus used for mixing . . 572
Oil drawn off from the solution of sodium phenolate . . . 575
Removal of impurities . . . 575
Decomposition by sulphuric acid . 578
by hydrochloric acid . . . 579
by sulphurous acid . . . 579
by nitre-cake 580
by carbonic acid 580
by sulphuretted hydrogen . . 582
Treatment of the crude carbolic acid 582
Properties of crude carbolic acid . 583
Waste water 583
The manufacture of pure crystallized carbolic acid 583
Distillation of the crude acid . . 583
Apparatus of Girard and Delaire . 585
Crystallization 588
Manufacture in Lancashire . . 588
According to Dr Ballard . . 591
Prevention of nuisance . . . 592
Preparation of absolutely pure carbolic acid 594
Synthetically 595
Treatment against reddening of the phenol 596
Causes of the reddening . . 596
Processes proposed for preventing it 598
Commercial cresols 600
Preparation of pure cresols . . 602
Properties of the three isomers . 602
Separation of the isomeric cresols . 603
Yield of pure products from crude carbolic acid 605
Analysis of carbolic acid . . . 607
Testing of crude carbolic acid . . 607
Analysis of pure carbolic acid . . 615
Fusing- or solidifying-point . . 616
Other tests 617
Quantitative estimation of phenol . 618
Koppeschaar's method . . . 619
Other methods 621
Estimation of the three isomeric cresols 623
Applications of carbolic acid . . 626
Statistical 628
Carbolic acid and cresol preparations 628
Carbolic-acid soaps 628
Creoline 629
Lysol 631
Other soapy preparations . . 632
Preparations of a non-soapy character 633
Carbolic-acid powders, etc. . . 636
Analysis of carbolic-acid preparations 637
Naphthalene 642
Recovery of crude naphthalene . 642
Refining it 643
Pressing 643
Distillation 645
Chemical washing 647

	PAGE
Naphthalene—*continued.*	
Second distillation	649
Special processes for refining naphthalene	650
Recrystallizing	652
Subliming	653
Examination of and for naphthalene	655
Uses of naphthalene	657
For artificial colours	658
For carburetting gas (albo-carbon light)	658
Other uses	661
Recovery of basic compounds from carbolic oil	663

CHAPTER X

LIGHT OIL AND CRUDE NAPHTHA

Light oil	665
Boiling-points	665
Components of light oil	666
Testing it	666
Applications of light oil as such	667
Rectification	667
Stills	671
Manufacture of benzoic acid from light oil	673
First runnings (light naphtha)	673
Boiling-points	674
Mode of taking these	675
Washing with chemicals	676
Functions of sulphuric acid	677
of alkali	678
Mixing apparatus	679
Operation of mixing	682
Treatment with sulphuric acid	683
Waste acid (acid-tar)	685
Washing with water	685
Washing with chemicals—*continued.*	
With alkali	686
Loss	687
Treatment with Nordhausen oil of vitriol	687
Other processes	689
Locality for carrying out the process	690
Treatment of the washed naphtha	690
Utilization of the waste acid (acid-tar)	692
For sulphate of ammonia	696
Examination of acid-tar	697
Recovery of the pyridine bases	698
from coal-tar itself	698
from acid-tar	699
Purification of crude pyridine	702
Testing it	703
For denaturing purposes	703
New employments of pyridine bases	705
of quinoline	706

CHAPTER XI

WORKING-UP THE LIGHT NAPHTHA INTO FINAL PRODUCTS

Rectification by steam	707
English steam-stills	708
Improvements	709
Working the stills	712
Principles of fractionation for the various commercial products	715
Self-acting control of fractional distillation	717
Various fractions obtained	719
Apparatus for a complete separation of the naphtha into pure benzene, toluene, xylene, etc.	722
Apparatus, etc.—*continued.*	
Coupier's still	722
Vedlé's rectifier	725
Savalle's apparatus	726
Heckmann's column	731
Other columns	734
Pure benzene, toluene, etc.	734
Removal of carbon bisulphide	735
Thiophen	736
Pure toluene	738
Xylenes	739

	PAGE
Composition and properties of the commercial descriptions of benzol and naphtha	741
German classification	742
Allen's results	744
Other statements	745
Commercial pure benzol	746
Testing benzols in the laboratory—	
1. Fractional distillation	747
Regnault's apparatus	747
English glass-retort method	748
Improved methods	752
German standard method	755
Influence of carbon bisulphide	759
2. Specific gravity	762
3. Test for paraffins (admixture of shale oil, etc.)	762
Distinctions between coal-tar benzol or naphtha from petroleum or shale-spirit	763
Nitrating test	765
4. Titration with bromine	766
5. Testing with concentrated sulphuric acid	767
6. Testing for the smell	768
7. Examination for carbon bisulphide	768
8. Testing for thiophen	772
9. Testing for total sulphur	774
10. Quantitative estimation of the pure benzenoid hydrocarbons in commercial benzols	774
Testing the commercial xylol for the three isomeric xylenes	777
Testing benzols in laboratory—*contd.*	
11. Practical tests in the laboratory for final products on a larger scale	779
Process employed at a large German works	779
by Claudon & Morin	782
by G. E. Davis	784
by Lunge	789
Storage and carriage of benzol, etc	791
Storing tanks	791
Arrangements to prevent explosions or fires	791
Carriage of benzol	793
Moving it by compressed air	793
Applications of benzol and naphtha	794
for colours and other organic preparations	794
as solvent and detergent	794
for indiarubber goods	795
for denaturing spirit of wine	796
as disinfectant	797
for carburetting gas	797
for illuminating purposes in the shape of burning naphtha and otherwise	800
for driving motors and motor cars	803
Various uses	804
Statistics of benzols	804
Fluctuations in their prices	805
Importation and exportation from Germany	806
Appendix I.—Synopsis of the products obtained from coal-tar	807
Appendix II.—Official rules to prevent accidents in tar-distillation works	808

CHAPTER XII

SOURCES FROM WHICH AMMONIA IS OBTAINED

Historical notes	810
A. Natural occurrence of ammonia	811
Guano	812
Soffioni	812
Volcanoes	821
In carnallite and other salts	821
B. Ammonia formed from the nitrogen of atmospheric air	815
General	815
B. Ammonia, etc.—*continued.*	
1. Application of high temperatures and of contact substances	816
of electricity	821
2. Synthesis of ammonia by means of nitrides	825
3. By means of cyanides, carbides, cyanamides	826

PAGE

B. Ammonia, etc.—*continued.*
Process of Margueritte and Sourdeval . . . 827
of Mond 828
of Brin 832
Other processes . . . 832
Process of Frank and Caro . 835
Development of the cyanamide industry 838
New processes . . . 839
Processes of the Badische Anilin- und Sodafabrik . 840
Scientific investigations . . 842
C. Ammonia formed in inorganic chemical manufactures . . 843
D. Ammonia from urine, sewage, etc. 844
E. Ammonia from guano . . . 851
F. Ammonia from bones, horn, leather, wool, hair, and other animal substances 851
G. Ammonia as a by-product in the manufacture of beetroot sugar and alcohol (molasses vinasse) . 856
H. Ammonia from peat . . . 861
I. Ammonia from bituminous shale . 870
K. Ammonia from coal . . . 871
Percentage of nitrogen in coal . 872
Ways of increasing the present production of ammonia . . 873

PAGE

K. Ammonia from coal—*continued.*
Value of ammonia for agriculture as compared with nitrate of soda 874
1. Production of ammonia in the manufacture of coal-gas . . 875
Yield of ammonia in the manufacture of coal-gas . . . 876
Special processes for the treatment of coal-gas, etc., for ammonia, Feld's processes . . . 882
Processes for increasing the yield of ammonia in gas-making . . 882
by lime 884
by hydrogen 884
by steam 885
Ammonia, etc., recovered from coal-gas directly, without scrubbers 886
Ammonia from the spent oxide of iron of gas-works . . . 887
2. Production of ammonia by treating coal or shale with steam . . 888
Process of Young and Beilby . 888
Other processes 892
The Mond gas process . . . 893
Other processes of this kind . . 900
3. Ammonia from coke-ovens . . 902
4. Ammonia from blast-furnace gases 908
5. Ammonia from producer-gas . 914
6. Ammonia from ordinary products of combustion (coal-smoke) . 915

CHAPTER XIII

THE COMPOSITION AND ANALYSIS OF AMMONIACAL LIQUOR, AND PROPERTIES OF ITS CONSTITUENTS

Composition of ammoniacal liquor . 918
"Fixed" ammonia . . . 919
Table showing the properties and composition of gas-liquor, obtained from the same coal, but taken at different points in the condensing-plant . . . 921
Table of gas-liquor from different coals 922
Analyses by Mr Linder . . . 922
Distribution of sulphur in ammoniacal liquor 923
of cyanogen 923

Composition of ammoniacal liquor—*ctd.*
Ammonium salts in recovered sulphur from Claus kilns (gas-works and coke-oven liquors) . 924
Analyses by Mayer and Hempel . 924
Valuation of ammoniacal liquor . 926
by the hydrometer . . . 926
by chemical test 927
Direct titration (saturation test) . 927
Distillation test of total ammonia . 928
Azotometric test 932
Complete analysis of ammoniacal liquor 935

PAGE

Valuation of Ammoniacal liquor—*ctd.*
Method of Dyson 935
Methods of the alkali inspectors . 937
of Mayer and Hempel . . 941
Special methods for sulphides . 942
for phenols 942
Ammonia in spent oxide . . 944
Properties of ammonia and its technically important salts . . . 945
Ammonia 945
Anhydrous ammonia . . . 945
Decomposition of ammonia . . 947
Absorption by water . . . 949
Specific gravity of solutions . . 950

PAGE

Properties of ammonia and its technically important salts—*continued.*
Vapour-pressures 951
Other properties 951
Ammonium carbonates . . . 951
Ammonium sulphide . . . 956
Ammonium sulphocyanide (thiocyanate) 957
Ammonium cyanide . . . 958
Ammonium chloride (sal-ammoniac) 958
Ammonium sulphate . . . 959
Ammonium sulphite . . . 960
Ammonium nitrate . . . 960

CHAPTER XIV

THE WORKING-UP OF AMMONIACAL LIQUOR

Storing and separation from the tar . 961
Working-up gas-liquor without distillation 964
Direct saturation with acids . . 964
Treatment with calcium sulphate . 964
Removal of the cyanides from gas-liquor before distillation . . 966
Manufacture of ammoniacal compounds by distilling the liquor—
General remarks . . . 968
Question of boiling with or without lime (volatile and fixed ammonia) 968
Preparation of the milk-of-lime . 971
Use of other compounds for liberating the ammonia (magnesia, caustic soda, cerium oxide) . . . 973
Mode of heating the stills . . 974
Safety-valves 974
Various products made from raw gas-liquor 975
I. *Manufacture of Concentrated Gas-liquor* 975
Apparatus of Solvay . . . 975
of Grüneberg for direct firing . 978
of Grüneberg and Blum . . 981
Apparatus of the Berlin-Anhaltische Gesellschaft (Bamag) . . 981
Various apparatus . . . 988
Concluding remarks 989

II. *Manufacture of Pure Liquor Ammoniæ* 989
General remarks 989
Simple apparatus used in Manchester 991
Apparatus of Elvers and Pack . 993
of the Berlin-Anhaltische Gesellschaft (Bamag) . . . 996
of Hirzel 997
of Feldmann 998
of Mallet 998
other apparatus . . . 1000
Removal of H_2S and CO_2 without lime 1003
Apparatus of Pfeiffer . . . 1003
of Solvay 1004
of Julius Pintsch . . . 1005
Solid ammonia 1008
Carriage of liquor ammoniæ . 1008
Action on iron 1009
Testing of commercial liquor ammoniæ 1009
III. *Manufacture of Anhydrous Liquid Ammoniæ* 1011
Manufacture 1011
Carriage on board ship . . . 1011
Composition and analysis of anhydrous liquid ammonia . 1015

PAGE

IV. *Manufacture of Sulphate of Ammonia* 1017
Coffey's still 1018
Horizontal cylindrical stills . . 1024
Continuous saturation apparatus . 1026
Dutch apparatus 1028
Apparatus of Mallet . . . 1029
of Grüneberg 1034
of Grüneberg and Blum . . 1037
of Feldmann 1040
of Julius Pintsch . . . 1045
of Hirzel 1045
of Mallet (1884) . . . 1047
Various forms of ammonia stills . 1049
Ammonium sulphate free from cyanides 1052
Grossmann's process . . . 1052
Treatment of liquor in the cold state for removing hydrogen sulphide and carbon dioxide . 1056
Apparatus specially intended for working-up *sewage* . . . 1059
Apparatus of Mallet . . . 1060
of Lencauchez 1062
Arrangements for absorbing the vapours in sulphuric acid and finishing the sulphate . . 1065
Saturators 1065
Quality of the absorbing-acid . 1077
Treatment of the sulphate taken out of the saturator . . 1079
Prevention of nuisance from ammonia works 1079
1. Reception, transportation, and storage of ammoniacal liquor . 1079
2. Leakages about the apparatus . 1079
3. Treatment of the condensed water 1080
4. Waste liquor and lime-mud from the stills 1081

PAGE

Prevention of nuisance, etc.—*continued.*
Recovery of sulphocyanide and ferrocyanide from the waste liquor 1084
Grossmann's process . . . 1084
5. Gases and vapours given off in the saturator 1085
Injury caused by them . . 1086
Removal by a chimney shaft . 1086
by combustion . . . 1088
Use for the manufacture of sulphuric acid 1089
Recovery of sulphur in the free state by the Claus process . 1089
Treatment by combustion and absorption by calcium carbonate 1092
Burning with excess of oxygen . 1094
Absorption of H_2S by an oxide of iron purifier . . . 1095
Various processes . . . 1097
Smell arising during the evaporation of sulphate liquors . 1098
Table on the percentage of ammonia dealt with in the various processes for treating the foul gases . . 1098
Concentration of ammonium sulphate solutions 1100
Manufacturing sulphate of ammonia otherwise than from ammoniacal liquor 1101
Commercial sulphate of ammonia . 1101
Properties 1101
Blue colour 1102
Conditions of sale . . . 1103
Injurious action of sulphocyanide 1104
Action as fertilizer . . . 1105
Other applications . . . 1107
Statistics on the manufacture of sulphate of ammonia . . . 1107

CHAPTER XV

OTHER TECHNICALLY IMPORTANT AMMONIUM SALTS

Ammonium chloride (sal-ammoniac) . 1111
Former sources 1111
Direct saturation of ammoniacal liquor with hydrochloric acid 1112

Ammonium chloride—continued.
Manufacture of the chloride from the sulphate 1114
Other processes 1116

PAGE

Properties of the crude ammonium chloride 1120
Sublimation of sal-ammoniac . . 1120
Pure crystallized salt . . . 1124
Further purification 1125
Uses of ammonium chloride . . 1125
Ammonium fluoride 1126
Ammonium ferrocyanide . . . 1127
Ammonium sulphocyanide (thiocyanate) 1127
Ammonium carbonate . . . 1130
Ammonium nitrite 1136
Ammonium nitrate 1136
Ammonium persulphate . . . 1141
Ammonium perchlorate . . . 1141
Ammonium thiosulphate . . . 1141
Ammonium phosphate . . . 1142
Ammonium chromates . . . 1143
Ammonium acetate 1143

APPENDIX

Tables for reducing the specific gravity of liquids lighter than water to the normal temperature of 15°·5 C., = 60° F. . . 1144
Table for comparing the degrees of Baumé's, Cartier's, and Beck's hydrometers with the corresponding specific gravities, for liquids lighter than water . . 1145
Table for comparing the degrees of the Centigrade and Fahrenheit thermometers 1146

ADDENDA

Statistics on the production of coal-tar and coal-tar products in the United States 1147
Promoting the separation of tar from the hot gases of destructive distillation 1147
Condensation of tar from the gases obtained in the distillation of coal 1148
Recovery coke-ovens . . . 1148
Production of benzene or its homologues from petroleum . . 1148
History of benzol (benzene) . . 1149
Fluorine, indene 1149
Diphenylene oxides 1149
Bases in coal-tar 1150
Properties of pyridine . . . 1150
Lutidines (dimethylpyridines) in coal-tar 1150
Manufacture of lampblack from coal-tar pitch, etc. 1150
Removal of free carbon from tar . 1150
Explosions by the employment of air-pressure for moving tar oils . 1150
Preventing the boiling-over of tar-stills 1151
Testing the consistency of bituminous binders in the asphalt-paving industry 1151
Melting-point of pitch . . . 1151
Distinguishing natural asphalt from tar asphalt 1151
Antiseptic properties of phenols and of indifferent tar oils . . . 1152

ALPHABETICAL INDEX OF NAMES 1153
ALPHABETICAL INDEX OF SUBJECTS 1167

COAL-TAR AND AMMONIA

CHAPTER I

INTRODUCTORY

THE process of destructive distillation of organic substances (that is, of heating them beyond the point of decomposition without access of air) is carried on for several industrial purposes. The principal object may be either the dry residue, or the gases evolved, or else the condensed distillate. The latter nearly always separates into two distinct layers—one of which consists of the water pre-existing in the original substance, or formed from it during destructive distillation, holding in solution a portion of the distillate; the other is formed by the condensed products insoluble in water, appearing in the form of a more or less viscid, dark-coloured oil, in some cases lighter, in others heavier, than the watery distillate, and generally known by the name of *tar*.

According as the original materials differ, the products of their destructive distillation differ also; but the difference is much greater in the condensed distillates than in either the solid residue or the permanent gases. The *solid residue* (charcoal, coke) was formerly considered to consist essentially of carbon and ashes, but it is in reality a mixture of compounds, containing very much C with but little H and O and sometimes N, perhaps also a little free C. The different qualities of wood-charcoal, coke, bone-charcoal, etc., are principally caused by the various descriptions and quantities of mineral matter intimately mixed with the "carbon" remaining behind as the residuum of the organic matter, and varying according to the original substance. Along with this it should not be overlooked that the process of destructive distillation is industrially carried on

BIRMINGH

at very different temperatures, by which both the physical nature and the chemical composition of the carbonaceous residue is greatly modified. Probably this plays at least as important a part as the difference between the original materials. It is also very possible that the molecules of carbon in wood-charcoal, coke, etc., do not consist of the same number of atoms. In any case it cannot be denied that the *combustible* portion of all carbonaceous residues, so far as the chemical reactions throw light upon it, does not present any great diversity.

The same may be said of the *permanent gases* formed in destructive distillation, part of which remains dissolved in the products of condensation. Carbon dioxide, carbon monoxide, nitrogen, hydrogen, the lowest members of the paraffin series and of the hydrocarbons containing less hydrogen (ethylene, acetylene) are always found. Sulphuretted hydrogen does not occur in the distillation of wood, but occurs regularly in that of coal and of animal matters. The production of these permanent gases for illuminating purposes is the object of a highly important industry, that of the manufacture of illuminating gas, in which now more than ever *coal* predominates almost to the exclusion of all other raw materials, except for very special purposes.

On the other hand, the *watery distillates* differ very much according to the nature of the raw material. In the case of wood, which contains very little nitrogen, these products are of an acid nature, acetic acid being the most important, next to which come methylic alcohol and acetone. The products originating from fossil vegetable substances behave in this respect similarly to wood, if they have been formed in the present or the more recent geological periods—for instance, peat and browncoal (lignite). The acid reaction of the distillate is frequently quoted as a criterion for distinguishing browncoal from real coal. All the methylic alcohol and most of the acetic acid of commerce are obtained from this source. Real coal, on the other hand, which always contains a certain amount of nitrogen, invariably furnishes a watery distillate whose reaction is strongly alkaline, owing to the presence of ammonia and, to some extent, of volatile organic bases. The bulk of ammonia and ammonia-salts comes from this source, viz., the gas liquor, *i.e.*, the ammoniacal liquor of gas-works, which is obtained not merely by cooling, but also by washing of the gas in the scrubbers.

A similar difference exists in the oily distillates, the *tars*. By "tar" we designate all those products of the destructive distillation of organic substances (whether produced by ourselves or by some natural process in these or in former times), which are not miscible with water. They are oily, more or less viscid, of a dark-brown up to a deep black colour, and a peculiar smell. According to the origin of tars, there are great differences among them, both physically and chemically. We may say, generally, that the tar from peat, browncoal, and bituminous shale consists *principally* of hydrocarbons of the "fatty" series, wood-tar of phenols and their derivatives, and coal-tar, on the other hand, principally of "aromatic" hydrocarbons. But along with the principal constituents there is always a large number of other compounds present: and matters are still further complicated by the fact that through the action of heat the individual compounds are transformed partly into other compounds of the same series, partly into compounds belonging to other series. Owing to this, tar obtained from the same material differs very much in composition according to the temperature of the dry distillation—nay, even according to the shape of the retorts, which allows the vapours to remain for a greater or less time in contact with the hot sides of the vessel—matters on which we shall speak in detail further on.

This explains why the tars are extremely complex mixtures. Acids (phenols) and bases can be extracted from it by "serial reactions"; but the great bulk of indifferent hydrocarbons can only be separated from one another by fractional distillation, only a few of them by crystallization or by the formation of sulphonic acids, etc. Of these operations the first is often insufficient for isolating the simple compounds, especially those of high boiling points, since at the boiling temperature the compounds are frequently decomposed, a drawback which can certainly be lessened by employing a vacuum, and thus reducing all the boiling points.

The tar from *browncoal* (lignite), as well as that obtained from peat and bituminous shale (and formerly also from the Torbane-Hill mineral), is manufactured for its own sake as a principal product, and forms the basis of the West-European industry of mineral oils and paraffin, which has proved its vitality even against the enormous competition of American

and Russian petroleum, of ozokerite, and of other products found in nature. The other products of the destructive distillation of similar more recent fossil substances possess very little or no value, except in the case of some very dense, coal-like browncoals, which furnish good coke and good gas, but no mineral oil. On the contrary, *coal-tar* up to the present is not manufactured as a principal product, the other products playing an inferior part: it is only an accidental but unavoidable by-product of the destructive distillation of coal for the purpose of manufacturing illuminating gas or coke, just as ammoniacal gas-liquor is. It is imperative to condense these two substances in order to purify the gas; but whilst the coke remaining behind in gas-making was always a by-product of considerable value, which materially influenced the cost price of the gas, tar and ammoniacal liquor were for many years regarded as refuse products which were not merely without value, but caused considerable inconvenience and expense for their removal. But since during the last fifty years, coal-tar and ammoniacal liquor have become starting-points for a chemical industry of enormous extent, they have also become factors contributing very greatly to the revenue of gas-works; and it can hardly be denied that circumstances might occur in which these two substances would be the principal products of the dry distillation of coal, so that the gas would only appear as a secondary product. It is of historical interest that the first English patent referring to the destructive distillation of coal (that of John Joachun (*sic*) Becher and Henry Serle, dated August 19, 1681) does not treat of the manufacture of lighting-gas, but of "a new way of makeing pitch, and tarre out of pit coale, never before found out or vsed by any other."

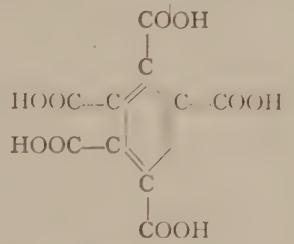
We shall see further on that during the last few years the production of tar and ammonia as principal objects of the distillation of coal has been the subject of trials carried out on a large scale.

Theory of the Formation of Coal-tar.

Before approaching this subject, we should be acquainted with the *chemical structure of "coal"* itself, but we are almost entirely in the dark on this subject. Kekulé (as pointed out by Bredt, *Z. angew. Chem.*, 1899, 950) derived it from

benzolhexacarbonic acid, that is, mellithic acid, which is formed on the oxidation both of amorphous carbon and of graphite; hence he claims these as "aromatic" substances, *i.e.*, benzene derivatives. The molecule of carbon, concluding from its infusible and non-volatile nature, must needs consist of a somewhat considerable number of atoms, and the formation of mellithic acid by the oxidation of carbon leads us to assume the molecule of carbon to consist of 12 atoms, probably arranged in this manner:—

Carbon.



Mellithic acid.

In a similar manner hexamethylbenzene is also converted by oxidation to mellithic acid, the ammonium salt of which acid has indeed been found in some coals.

We cannot here go further into the extensive literature on the formation and the probable constitution of coal, and we merely refer to the following papers:—Guignet (*Comptes rend.*, vol. 88, p. 590); Frémy (*ibid.*, p. 1048); Baltzer (*Vierteljahrsschr. d. Zürcher Naturf. Ges.*, 1875); Muck (*Steinkohlenchemie*); Friswell (*Chem. Zeit.*, 1892, p. 204); Watson Smith and Chorley (*J. Soc. Chem. Ind.*, vol. 12, p. 220); Reinsch (*J. prakt. Chem.*, 1880); Siepmann (*Chem. Zeit. Rep.*, 1891, p. 86); Kronberg (*Z. angew. Chem.*, 1899, p. 952); F. Fischer (*ibid.*, pp. 790, 949, 952); Kraemer (*Berl. Ber.*, 1890, pp. 84, 3169, 3269, 3276); Russig (*Z. angew. Chem.*, 1899, p. 950).

The theory of the formation of tar in the distillation of coal is too uncertain to be treated at length in this place. We know from the researches of very many chemists, beginning with Priestley, the most prominent of whom is Berthelot, that most organic bodies, also those of the fatty series, furnish aromatic compounds (benzene and its homologues, naphthalene, anthra-

cene, etc.) when exposed to a very great heat, especially when brought into contact with a red-hot or white-hot tube. But, on the other hand, those same aromatic products are decomposed by higher degrees of heat, and ultimately furnish free hydrogen, along with free carbon, or else compounds so rich in carbon that they have been hitherto indistinguishable from it. The different stages of these processes are extremely complicated, and the attempts at explaining the formation even of the better known constituents of coal-tar by means of some plain reactions of a few simple compounds, such as acetylene, allylene, etc., do not seem to be very convincing. The problem of the theory of destructive distillation has been approached from a different side by E. Mills (*J. Soc. Chem. Ind.*, 1885, p. 325). His argument turns upon the point that the process by which cellulose, $nC_6H_{10}O_5$, is turned into coal is essentially one of dehydration; so that, for instance, by heating wood to 430° without pressure, the residue has the composition nC_6H_2O; and he assumes that in any case the organic matter in coal, shale, etc., corresponds to an initial symbol nC_6 or $2nC_3$; also that a definite relation exists between the C of the fixed carbon on the one hand and the C of the gas+tar on the other, in which C_3 is always the fundamental unit. We must refer for details to the original, merely pointing out two oversights in that reasoning (which, of course, were quite well-known to the author), namely, that woody fibre is not at all $= nC_6H_{10}O_5$, the formation of oxycellulose, lignin, etc., having intervened, and that the formation of coal from woody fibre is anything but a mere dehydrating process, $-CO_2$, CO, CH_4, and other carbon compounds being liberated at the same time as water.

More recently the following papers have appeared on the formation of tar: Spatjew (*Chem. Zeitschr.*, I., 360); Werner von Bolton (*Z. Elektrochem.*, 1902, 166).

Historical Notes on the Application of Coal-tar and the Products obtained therefrom.

Before the latter part of the seventeenth century no notice seems to have been taken of the appearance of tar during the heating of coal—a substance of comparatively small importance at that time. One of the pioneers, if not the real originator, of

the industry of coal-tar, the German chemist Johann Joachim Becher, describes his observations in the following words[1]:—

"In Holland they have peat and in England pit-coals [Steinkohlen]; neither of them is very good for burning, be it in rooms or for smelting. But I have found a way, not merely to burn both kinds into good coal [coke] which not any more smokes nor stinks, but with their flame to smelt equally well as with wood, so that a foot of such coal makes flames 10 feet long. That I have demonstrated with pit-coal at the Hague, and here in England at Mr Boyle's, also at Windsor on the large scale. In this connection it is also noteworthy that, equally as the Swedes make their tar from firwood, I have here in England made from pit-coal a sort of tar which is equal to the Swedish in every way and for some operations is even superior to it. I have made proof of it on wood and on ropes, and the proof has been found right, so that even the King has seen a specimen of it, which is a great thing in England, and the coal from which the tar has been taken out is better for use than before." We have seen above (p. 4) that Becher protected his invention by letters-patent.

Later on Clayton (1737-38) made some statements on the nature of the products obtained by destructive distillation; besides coke and tar he found that combustible gases were formed at the same time.

About the middle of the eighteenth century the use of coal became more general, and more especially the manufacture of coke for smelting purposes, in lieu of wood-charcoal, began to be practised on a more extensive scale. It is most remarkable that, in the infancy of coke-making, the recovery of tar in that process was already practised, which has only during the last few years again come to the fore. A French metallurgist, de Gensanne, describes and figures a kind of muffle-furnace for coking coal and recovering tar, which was working at Sulzbach, near Saarbrücken, before the year 1768.[2] From the description of the tar

[1] "Närrische Weisheit, No. 36," quoted by G. Schultz, *Chemie des Steinkohlentheers*, 2nd ed., p. 5, and faithfully translated here.

[2] De Gensanne, *Traité de la fonte des Mines*, Paris, 1770, vol. i., ch. 12, quoted by Gurlt, *Die Bereitung der Steinkohlen-Briquettes*, 188, p. 22. The place is called "Fischbach" here, but "Sulzbach" occurs in the communications made by Gurlt to Mr Watson Smith, and quoted in the *J. Soc. Chem. Ind.*, 1884, p. 602.

or "oil" obtained at Sulzbach (it is said to resemble distilled petroleum, and was used for burning in peasants' and miners' lamps), it must have been much nearer in quality to the blast-furnace and the "Jameson" tar (to be mentioned hereafter) than to gas-tar or to the tar nowadays obtained from closed coke-ovens. Gurlt points out that the "Kohlenphilosoph" Stauf (a visit to whose lonely forest cottage near Saarbrücken, in 1771, is vividly described by Goethe, then a student of Strasburg University) seems to have been the originator of that coking-process; he produced from it "oil," bitumen, lampblack, and had also collected a cake of sal ammoniac from the "burning hill" near by.

One of the patents of that indefatigable inventor, the Earl of Dundonald (No. 1291, of April 30, 1781), describes an invention for coking coal, intituled, "A method of extracting or making tar, pitch, essential oils, volatile alkali, mineral acids, salts, and cinders from pit-coal." The condensation of the volatile portion is effected by mixing steam with it and then applying cold water. This invention does not, however, seem to have been worked out on a large scale; at any rate it must have soon fallen into disuse.

In any case it is certain that the manufacture of coal-tar was never carried out on any extensive scale until it appeared as a necessary by-product in the manufacture of illuminating-gas from coal, the idea of which seems to have occurred, towards the end of the last century, at the same time to the Frenchman Lebon and the Englishman William Murdoch. The former had already recommended the use of tar for preserving timber; but it was the latter who, along with his celebrated pupil Samuel Clegg, really laid the foundation of the enormous industry of gas-making. The first private gas-works was erected in 1798, at the engineering works of Bolton and Watts; the first public gas-works in London in the year 1813, in Paris 1815, in Berlin 1826.

The tar formed in the manufacture of coal-gas necessarily forced itself upon the notice of the gas-manufacturer, since it could not be thrown away without causing a "nuisance." It was probably from the first burnt under the retorts; but the method of doing this without giving very much trouble was not understood then. Other quantities, no doubt, were used, in lieu

of wood-tar, as a cheap paint for wood or metals; but it must have been soon found out that in the crude state it is not well adapted for this purpose, as will be shown later on. It was also quickly perceived that in this respect tar is improved by boiling it down to some extent; and as early as 1815 Accum showed that, if this boiling down is carried out in closed vessels (stills), a volatile oil is obtained which may be employed as a cheap substitute for spirits of turpentine. But this distilling-process does not seem to have been carried out to any great extent; and coal-tar remained, for more than a generation from the first introduction of gas-lighting, a nuisance and hardly anything else.

In Germany the first more extensive employment of gas-tar was for making roofing-felt (which had already before then been made in Sweden by means of wood-tar), for which purpose it has to be deprived of water and the more volatile constituents. Instead of condensing these, they were at first almost everywhere, and later on in many cases, removed by evaporating the tar in open vessels, thus creating a considerable risk from fire. In Germany, Brönner, of Frankfort, was the first (in 1846) to treat the tar for this purpose in a still, and to condense the more volatile tar-oils, from which he prepared a detergent, long after known by his name, and consisting principally of benzene.

In England, where the manufacture of illuminating-gas originated, and where it has always been, and still is, carried on to a very much greater extent than on the Continent, a more extensive industrial employment for coal-tar was first opened out by the invention of Bethell (1838) for preserving timber, especially railway-sleepers, by impregnation with the heavy oil distilled from gas-tar. From that time dates the introduction of tar-distilling on a large scale. The light oils may have been lost even here in some cases; but more usually they were condensed and employed as "coal-tar naphtha" for burning and for dissolving indiarubber.

The day of the light tar-oils came after A. W. Hofmann (1845) had shown the presence of benzene in them, but especially when Mansfield (whose researches will be mentioned in detail hereafter), in his patent-specification (1847), for the first time accurately described the composition of these oils, along with a process for preparing benzene in a pure state and on a large scale, and with proposals for utilizing the tar-oils of lowest

boiling-point for lighting purposes. The industrial preparation of benzene was soon followed by that of nitrobenzene, at that time only employed as a substitute for the essential oil of bitter almonds, and known by the French fancy name "essence de Mirbane." But all these applications produced only a limited demand for the light oils which could be made from the rapidly increasing quantities of gas-tar; so that the latter, except in a few instances locally, did not attain any considerable commercial value. But a sudden impetus was given to tar-distilling in 1856 by the discovery of the *aniline colours*, the material which forms their starting-point, benzol, being exclusively derived from coal-tar.

In the centres of industry, where at the same time most gas is made, coal-tar was at once converted from a nuisance into a commercial article in great demand at good prices. Although only about one per cent. of the tar is obtained as benzol, this article at first yielded so much profit that the other products of tar-distilling could be sold at low rates and new markets could be opened out for them. It is true that, as usual, excessive competition led at one time to a great fall in the price of benzol; and as at the same time the sale of creosote-oil and pitch was very poor, tar-distilling seemed to be hardly a remunerative business. But this condition of things passed away. Even at that time a more rational utilization of the by-products permitted working at a profit; and this, so long as tar was at a reasonable price, was fully secured when, through Graebe and Liebermann's discovery of artificial alizarin, anthracene attained a much higher value than any other product from coal-tar.

In the course of time the following state of affairs has established itself. In England, where by far the largest quantity of gas-tar is produced, where benzene was discovered by Faraday, its industrial preparation by Mansfield, the first aniline colour by Perkin, and where the conditions are the most favourable for the purchase of the necessary chemicals as well as for the sale of the colouring-matters, the manufacture of artificial dyes has only risen to moderate dimensions. The same has been the case in France. On the other hand, in Germany and Switzerland the manufacture of coal-tar colours has been established on an enormous scale, so that the tar produced there formerly could only supply a small portion of the benzol and anthracene required, most of it being imported from England and France,

partly in the form of aniline. But the employment of the other coal-tar products, especially dead oil and pitch, in Germany has by no means increased *pari passu* with that of benzol and anthracene; the former, very cheap, articles frequently have to seek markets at such distances that the expense of carriage becomes excessive. Moreover, gas-making in Germany is only partially concentrated at a few large centres of industry; very many small gas-works are scattered all over the country, sometimes not even situated near a railway line, and hardly ever on the bank of a canal or navigable river; so that the collecting of tar for a larger tar-distillery does not pay. Hence, up to a short time ago, in Germany and Switzerland, where the manufacture of coal-tar dyes has reached its greatest development, it has happened that the tar produced at the gas-works has to be burned under the retorts, a state of things which sometimes has partially, but from other causes mentioned before, arisen in Great Britain as well.

Quantity of Coal-tar produced.

For the earlier statistics on the quantity of coal-tar produced we must refer to the previous editions of this treatise, and we give here only a few notes on this subject, but the recent statistics will be given at greater extent.

In 1883 it was estimated that the coal-tar then produced at gas-works amounted to

450,000	tons in	Great Britain
85,000	„	Germany
75,000	„	France
50,000	„	Belgium
15,000	„	Holland
675,000	tons.	

For 1885, Mr Wilson, of the Beckton tar-works, puts the quantity of coal-tar distilled in the United Kingdom at 643,000 tons.

In 1886, the quantity of coal-tar distilled in Holland was 20,000 or 22,000, in Belgium 30,000 tons.

In the United States, in 1886, according to A. von Schauer, 120,000 tons of tar were produced, of which 60,000 were distilled (this seems to be an excess of the reality), 37,000 tons were used in the manufacture of roofing-paper, and 23,000 tons used in the raw state.

From that time onward the tar produced in other industries than that of gas comes more and more to the front, principally that obtained in by-product coke-ovens and blast-furnaces, about which details will be given in the next chapter.

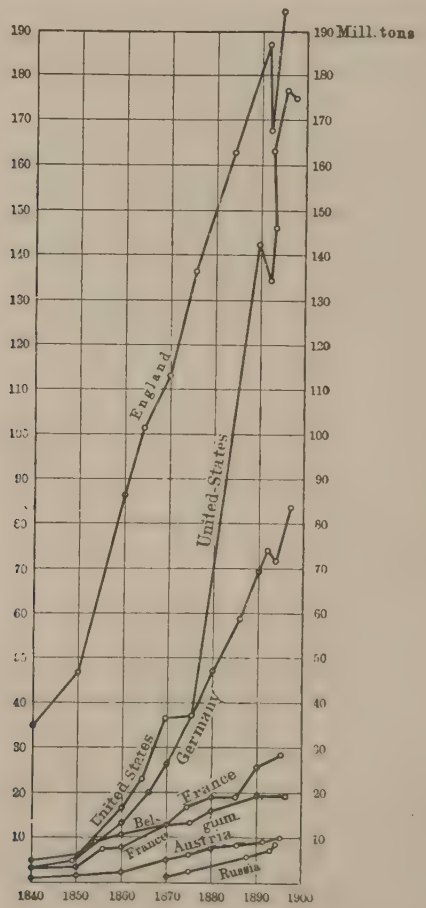


FIG. 1.

Dr Bueb, Chemist-in-chief of the Dessau Continental Gas Company, supplies the following estimate of the quantity of coal

used for the manufacture of gas in Europe during 1898, to which we add the corresponding yield of tar, at the estimate of about 5 per cent.:—

	Coal distilled, tons.	Tar produced, tons.
Great Britain . .	13,333,000	666,650
Germany . . .	3,333,000	166,650
France	2,700,000	135,000
Austria-Hungary . .	830,000	41,500
Scandinavia . . .	433,000	21,650
Belgium . . .	400,000	20,000
Italy	333,000	16,650
Russia	333,000	16,650
Holland . . .	300,000	15,000
Denmark . . .	270,000	13,500
Switzerland . . .	135,000	6,750
		1,120,000

The diagram, Fig. 1, is interesting as showing the development of the production of coal from the year 1840 to 1897, which to a considerable extent must keep pace with the production of coal-tar from various sources.

We now give the statistics for the last ten years. Beilby in a most interesting and suggestive address (*J. Soc. Chem. Ind.*, 1899, p. 647), gives the following statistics concerning the distillation of coal in the United Kingdom at that period:—

	Coal distilled.	Coke produced.	Tar produced.	Sulphate of Ammonia.	Gas produced.
	Million tons.	Million tons.	Tons.	Tons.	Million cub. feet.
At Gas-works . .	13	7-8	650,000	130,000	130,000 at 650 B.T.U. per cub. ft.
„ Blast-furnaces .	2	...	150,000	18,000	360,000 „ 130 „
„ Recovery coke-ovens . .	1¼	0·9	62,000	11,000	12,500 „ 600 „
„ Shale-oil works .	...	...	...	37,000	...
If the beehive ovens were entirely replaced by recovery-ovens, there would be a further production of . . .	...	...	862,000	196,000	...
	...	9	620,000	110,000	125,000

The 862,000 tons of tar now produced are distilled and separated into 474,000 tons pitch and 345,000 tons oils. The increase of these quantities, if not merely all coke were made in recovery-ovens, but also the 130 million tons of coal now burned in the raw state were to be distilled, could not be disposed of in the present way. Beilby discusses the possibilities in that direction, and thinks that the manufacture of briquettes (patent fuel) from the coke would greatly extend and would yield a smokeless fuel. The sulphate of ammonia would more and more take the place of Chilian nitrate of soda. The tar oils not consumed by other industries would serve as smokeless fuel.

Schniewindt (*Min. Ind.*, X., 152), gives the following estimate of the production of coal-tar in 1901, based on that of ammonium sulphate and gas:—

	Tons.
United Kingdom	908,000
Germany	590,200
United States (including Water-gas tar)	272,400
France	190,680
Belgium, Holland, Sweden, Norway, Denmark	272,400
Austria, Russia, Spain, and other European countries	199,760
All other countries	227,000
	2,660,440

Russig, in several papers contributed to the *Chemische Zeitschrift*, estimates the total quantity of coal-tar produced as follows (in tons):—

	In 1900.	In 1901.	In 1902.
United Kingdom, Gas-tar	692,000	742,000	755,000
„ Blast-furnace tar	150,000	128,000	156,900
„ Coke-oven tar	85,000	95,000	122,000
„ Total	927,000	965,000	1,033,900
Germany, Gas-tar	180,000	180,000	...
„ Coke-oven tar	300,000	270,000	...
„ Total	480,000	450,000	...
United States, Gas-tar	60,900	(?)	(?)
„ Coke-oven tar	47,500	50,500	60,100
„ Water-gas tar	202,100	(?)	(?)
„ Total	310,500	...	...

	In 1900.	In 1901.	In 1902.
France, Gas-tar	144,000	...	...
„ Coke-oven tar . . .	35,000	...	...
„ Total	179,000	180,000	...
Other European states . . .	355,000	375,000	...
All the world over	2,270,500	...	...

The same author (*Chemische Zeitschrift*, III., 180) estimates the production of coke-oven tar alone in the United States at 75,000 tons for 1903, at 125,000 tons for 1904. Dr Köhler (private information) estimates the production of coke-oven tar in the United States, from 2286 United-Otto ovens and 1320 Semet-Solvay ovens, at 300,000 tons, to which must be added 300,000 tons of tar from gas-works which, however, to a great extent do not furnish ordinary coal-tar, but water-gas tar. Another 1500 ovens were to be built by the U.S. Steel Corporation. Only about 20 or 30 per cent. of the tar produced in the United States finds it way into the distilleries.

In the year 1905, according to *Census Bulletin No.* 92, p. 43, the production of tar in the United States was:—

77,643 tons ordinary gas-tar.
259,934 „ water-gas tar.
131,117 „ coke-oven tar.

For Germany, Haarmann (*Glückauf.*, 1906, p. 421) gives in detail the figures for the production of coke-oven tar (see later on) from 1897 to 1904, in which year it reached 175,863 tons in the Ruhr district, and 276,805 tons for all Germany —against only 18,000 tons in 1887. To this must be added the gas-works tar, estimated by Bunte at 225,000 tons for 1904, thus yielding a grand total of 500,000 tons. For 1906 Köhler estimates the quantity of coal-tar worked up in Germany at 600,000 tons, for 1907 at 675,000 tons from all sources. For 1908 Dr Spilker (private communication) estimates the quantity of tar used in Germany at 900,000 tons, of which 700,000 tons are got westwards of the Elbe.

Special statistics on the production of tar from coke-ovens will be given in Chapter II.

CHAPTER II

PROCESSES FOR OBTAINING COAL-TAR

A. *The Production of Coal-tar at the Gas-works.*

FORMERLY nearly the whole of the coal-tar was obtained, and the greater part of it is so now, as a by-product in the manufacture of ordinary coal-gas for illuminating purposes, and formerly, therefore, the denominations "coal-tar" and "gas-tar" were practically identical and were both in constant use. Since the manufacture of coal-tar from other sources has become practicable, we must distinguish as "gas-tar" that particular kind of coal-tar which is obtained in the process of gas-making as an involuntary by-product.

It is not within the scope of this treatise to give a description of the ordinary contrivances for condensing the tar, which belong entirely to the domain of gas-making. It is sufficient to mention that the constituents of the tar escape from the gas-retorts in the form of vapour, with a little solid free carbon in an extremely finely divided state; they are precipitated in the hydraulic main, in the condensers, scrubbers, etc., in a liquid state, at the same time as the ammoniacal liquor is formed. In one particular instance,[1] of 100 parts of tar altogether obtained, there was found 61·6 in the hydraulic main, 11·8 in the condenser, 26·6 in the scrubbers. The tar formed in the hydraulic main is, of course, poorer in the more volatile products than that formed in the condensers and scrubbers, and is consequently much thicker than the latter; but it is usual to mix all these descriptions of tar in the cistern where they collect, along with the ammoniacal liquor.

The quantity, and to a much greater extent the quality of the tar are influenced by the *nature* of the *raw material*

[1] Schultz, *Steinkohlentheer*, 2nd ed., i., p. 43.

and by the *temperature* at which the decomposition of the coal is carried on. Some coals at low temperatures yield 16 gall. of tar, with 9000 cub. ft. of gas per ton of coal, whilst at high temperatures the same coal yields but 9 gall. of tar, with about 11,000 cub. ft. of gas.[1] If the temperature be comparatively low, mostly such hydrocarbons are formed as belong to the paraffin (methane) series, having the general formula C_nH_{2n+2}, along with olefines, C_nH_{2n}. The lower members of these series are liquid, and, furnished in the pure state, are lighting- and lubricating-oils; the higher ones are solid and form commercial paraffin. They are always accompanied by oxygenized derivatives of the benzene series (phenols); but of these the more complicated ones predominate, in some of which methyl occurs in the benzene nucleus, in others replacing the hydrogen of hydroxyl:—*e.g.*, cresol, $C_6H_4(CH_3)(OH)$; guaiacol, $C_6H_4(OH)(OCH_3)$; creosol, $C_6H_3(CH_3)(OH)(OCH_3)$, etc. Liquid products prevail; and among the watery ones acetic acid (which is again a compound of the fatty series) is paramount. Of course also permanent gases are always given off, though in comparatively small quantity.

If, on the other hand, the coal has been decomposed at a very high temperature, the molecules are grouped quite differently. Whilst the olefines and members of the acetylene series still occur more or less, the hydrocarbons of the paraffin series disappear almost entirely; and from them are formed on the one hand compounds much richer in carbon, on the other hand more highly hydrogenized bodies. The latter always occur in the gaseous state; hence the gas so produced contains methane or marsh-gas, CH_4, and free hydrogen as principal constituents, and is very much increased in quantity. The carbon thus set free is partly deposited in the retorts themselves, and then occurs in a very compact graphitoidal form; some of the free carbon occurs in a state of extremely fine division in the tar, and forms a constituent of the pitch or coke remaining behind from tar-distilling; another portion contributes to the formation of compounds richer in carbon, belonging to the "aromatic" series, all of which are derived from benzene, C_6H_6. At the same time the action of heat effects further molecular "condensations," usually with separation of hydrogen, by which process compounds

[1] Davis, *J. Soc. Chem. Ind.*, 1886, p. 5.

of a higher molecular weight are formed, as naphthalene, anthracene, phenanthrene, chrysene, etc. The never-absent oxygen must also in this case cause the formation of phenols; but here phenol proper, or carbolic acid, $C_6H_5(OH)$, predominates, whilst cresol and the other homologues are diminished in quantity, and the dioxybenzenes, as well as their methylated derivatives, disappear altogether.

These details will be made clearer when it is stated[1] that Zwickau glance-coal yielded the following quite different products, according to whether it was put in a cold retort and gradually brought to a red heat (*a*), or distilled quickly from a very hot retort (*b*):—

	a.	*b.*
Coke . . .	60	50
Water . . .	10·7	7·7
Tar	12	10
Gas and loss . .	17·1	32·1

The tar from *a* consisted of photogen, paraffin oil, lubricating-oil, paraffin, and creosote; that from *b*, of benzene, toluene, naphthalene, anthracene (together with heavy oils corresponding to the paraffin and lubricating-oil), and much creosote.

When coal is subjected to destructive distillation in coke-ovens, the temperature is considerably lower than in gas-retorts. Hence there is a great difference between the tars obtained in these processes. Thus Behrens[2] found that the tar obtained in the distillation of coal in the ordinary fireclay gas-retorts was much richer in benzene, toluene, naphthalene, etc., than the tar made in Pauwels's coke-ovens from the same kind of coal. The latter is of less specific gravity and contains more liquid (parraffinoid) hydrocarbons, also far more substances soluble in alkalis, but hardly any carbolic acid. We shall further on treat in detail of the differences between tars obtained in various processes of coal-distilling, carried on for other purposes than gas-making.

The same cause explains the difference between the tar of wood-gas-works, that of wood-vinegar-works, and that of charcoal-heaps (*Meilers*). The former, produced at a very high temperature, is black, thin, smells almost like coal-tar,

[1] From Stohmann-Kerl's *Chemie*, 3rd ed., vi., p. 1162.
[2] Dingler's *Polyt. Journ.*, vol. ccviii., p. 362.

and contains much real phenol, along with benzene, toluene, naphthalene, etc. The tar obtained at a lower temperature, especially that from the charcoal-heaps, contains mostly cresol and guaiacol in place of phenol, and paraffin instead of naphthalene; it has a lighter brown colour and a much milder smell.

A further difference between distillation at high and at low temperatures is stated to consist in the fact that most of the nitrogen appears in the former case in the shape of aniline and fatty amines (ethylamine, propylamine, amylamine); in the latter case in that of bases of the pyridine series, along with picoline, lutidine, viridine, etc. But this requires to be verified by more detailed investigations.

Of course it is not possible to obtain the above products in any desired quality from any one of the raw materials here alluded to, merely by altering the temperature of the dry distillation. It had, for instance, been doubted whether real benzene can be obtained at all by direct distillation from more recent deposits, as peat, browncoal, some sorts of bituminous shales, etc. This matter has been cleared up by Heusler (*Berl. Ber.*, 1892, p. 1665; 1895, p. 448), who proved that the distillate from lignite between 80° and 93° contains 34 per cent. benzene, and that between 100° and 110° 45 per cent. toluene; he also found the higher homologues up to cymene, naphthalene, thiophens, ketones, nitriles, and naphthenes; whilst in Scotch shale-oil he could find only traces of benzene and toluene and no naphthalene at all. At all events, these materials can in no case serve for a profitable extraction of benzene and the other aromatic hydrocarbons. Wigan cannel coal, if used alone, instead of, as is usual, being mixed with less bituminous coals, yields tars containing so much paraffin that no tar-distiller will take them (Watson Smith). On the other hand, photogen, paraffin oil, etc., cannot be profitably made from coal by distillation at a lower temperature;[1] for cases like that of the Zwickau coal, mentioned above, do not furnish a rule for industrial practice, which has proved that even among brown-

[1] Professor Dittmar, of Glasgow, informs me that about 1875, at Manchester, oils of the formula C_nH_{2n+2} were made by the distillation of coal at a low temperature. But no doubt this was cannel coal, which in that respect occupies a place between real coal and more recent fossils.

coals only certain light, earthy descriptions ("Schweelkohle") are adapted for the manufacture of lighting-oils. But we shall see that it is at least in our power, by *subsequent overheating*, to split up the fatty products (paraffins) from browncoal and petroleum, to a great extent, into gases and aromatic compounds; and to this, no doubt, the illuminating-power of oil-gas and the gas made from petroleum-residues is mainly due.

Our present task lies only with the treatment of real coal. We must remember that at a lower temperature less permanent gases and more methylated derivatives (toluene, xylene, higher phenols), at a higher temperature more gases, along with benzene, naphthalene, anthracene, and far more free carbon, are formed. At very high temperatures the tendency to complete dissociation becomes far more pronounced; the products approach more and more to free carbon on the one hand, and free hydrogen on the other; but this end itself is never actually reached at the temperatures attainable to us. Most gas-engineers try above everything to get as much gas as possible out of the coal, and therefore distil at the highest possible temperature. Up to a certain point this is quite rational, and is even unavoidable from the nature of the material now universally employed for gas-retorts, viz. fireclay. This point seems to be reached when the fatty compounds are split up as far as possible before any considerable separation of free carbon has taken place. Beyond this point more gas will be got, but its lighting-power will be less; the tar will at first contain rather less anthracene, and more naphthalene, which has much less value, also more phenanthrene, pyrene, chrysene, diphenyl, etc., which are at present valueless; so that its value on the whole will be less. There is also a reduced quantity of tar, if the temperature in the retorts is raised higher. The separation of free carbon in the retorts and the tar is also largely increased. In England the usual temperature of working seems now to be about 1100° C. (= 2000° F.). But, properly speaking, it should be experimentally ascertained (and that for every class of gas-coal specially) at what temperature the maximum of lighting-power is obtained, even if concentrated in a smaller volume of gas, and also at what temperature we can get a maximum yield of benzene, toluene, phenol, and anthracene in the tar. Probably the two

maxima will not coincide; and it will then be a matter of business calculation whether the one or the other is to be worked for. It is evident that the market prices of the tar-products will influence this consideration largely, and that any diminution in the price of gas will turn the scale in favour of richer tar.

It is quite certain that the composition of coal-tar was very different from what it is now at the time when coal used to be distilled in cast-iron retorts, necessarily at a considerably lower temperature than the above-mentioned 1100° C., which applies to fireclay retorts. The higher temperature existing in the latter is certainly to some extent counterbalanced by the action of the exhauster, which causes the gases to remain a shorter time in contact with the heated sides of the retort. The exhauster also makes the tar thicker, by carrying away a good deal of coal-dust from the retort in a mechanical way.

L. T. Wright (*J. Soc. Chem. Ind.*, 1886, p. 559) states that as the distillation-temperature is increased the tar decreases slightly in quantity, but increases in specific gravity. Above a certain temperature, which differs for each kind of coal, the trouble caused by thick tar stopping up pipes, etc., prevents the gas-making process from being carried on. In the average of gas-works the distillation-temperature is as high as can be conveniently attained with the present form of gas-making plant, so that there is practically no margin for any reduction in the output of tar by the employment of higher "heats."

The following table serves to illustrate the variations in the volume and weight of tar (and gas) yielded by coals distilled at

Description of Coal.	Temperature of distillation.	Cubic feet of gas per ton.	Gallons of tar per ton.	Spec. grav. of tar.	Lb. of tar per ton.	Weight per cent. on coals.
Derbyshire Black Shale, No. 1 .	very high	11,128	10·63	1·210	128·62	5·74
" " " .	normal	10,400	...	1·185	...	...
" " " .	very low	7,856	11·50	1·145	131·67	5·88
Derbyshire Black Shale, No. 2 .	very high	11,190	12·01	1·207	144·96	6·47
" " " .	normal	10,400	...	1·185	...	...
" " " .	very low	7,562	14·38	1·136	163·35	7·29
Notts Top Hard Cannel . .	normal	9,852	21·32	1·147	244·54	10·92
" " . .	very low	7,125	23·81	1·116	265·72	11·86

widely different temperatures. The experiments were conducted in clay retorts with the ordinary form of gas-plant. The expression "normal temperature" means the highest practically and continuously possible in a modern gas-works; by "very high temperature" is meant one only practicable by careful nursing and for a short period.

Later on (*J. of Gas Lighting*, 1888, p. 169) the same author made the following statements:—

Derbyshire Silkstone coal, of the following composition: C = 75·71; H = 6·27; S = 1·72; N = 1·72; O = 11·59; ashes = 2·99, yielded, on carbonization, for each 100 kg. of tar:—

At about 800° C.: 64·75 kg. coke and 6·43 litres tar, spec. grav. 1·0, with about 15 per cent. free carbon;

At about 1100° C.: 64·16 kg. coke and 5·37 litres tar, spec. grav. 1·207, with about 25 or 30 per cent. free carbon.

The same writer (*J. Soc. Chem. Ind.*, 1888, p. 59) examined the composition of tar, yielded by the same kind of coal (C = 81·92; H = 5·39; N = 1·28; S = 1·97; O = 6·88; ashes = 2·56) at different carbonizing temperatures, between 600° and 800° C.:—

	I.	II.	III.	IV.	V.
Cubic feet of gas yielded per ton of coal	6600	7200	8900	10,162	11,700
Spec. grav. of tar	1·086	1·102	1·140	1·154	1·206
Composition of tar per cent. weight:—					
Ammoniacal liquor	1·20	1·03	1·04	1·05	0·383
Crude naphtha	9·17	9·65	3·73	3·45	0·995
Light oil	10·50	7·46	4·47	2·59	0·567
Creosote oil	26·45	25·83	27·29	27·33	19·440
Anthracene oil	20·32	15·57	18·13	13·77	12·280
Pitch	28·89	36·80	41·80	47·67	64·080

We see that with the rise of temperature the yield of naphtha and light oil sinks from 20 per cent. to 1·5 per cent., and that of pitch rises from 29 per cent. to 64 per cent. The yield of benzol from the crude naphtha (boiling up to 100 C.) fell with the rise of temperature, whilst naphthalene increased. The crude naphtha of the light tars contained up to 5·0 volume per cent. of liquid paraffins, that of the heaviest tar only 1·0 vol. per cent. Anthracene seems to be formed mostly at medium temperatures; the

maximum 0·370 per cent., was found in tar of spec. grav. 1·140, whilst the lighter and heavier tars contained less of it.

This agrees with Kraemer's experience (*J. Gasbeleucht.*, 1887, p. 849) that tar distillers prefer the tar from smaller gas-works, whose retorts are fired with coke, to that from large gas-works, provided with gas-producer fires and working at higher temperatures.

Watson Smith (*J. Soc. Chem. Ind.*, 1889, p. 950) relates similar observations. With the rise of temperature he found in the tar more naphthalene and anthracene. The carbolic acid appeared not merely in the middle oils, but also in the heavy oils, from which it can be recovered by Lowe's patent No. 3005, of 1872.

Hilgenstock (*J. Gasbeleucht.*, 1902, 617) attributes the notorious difference between gas-tar and coke-oven tar with respect of their contents of free carbon and other products of pyrogenetic decomposition to the fact that in coke-ovens the escaping vapours do not attain temperatures above 600° C., and that they are moreover protected against decomposition by the dilution of the heavy vapours, slowly given off from the interior of the coal block, with the fire-resisting gases escaping at the same time from the outer zone of the block. On the other hand, in the case of gas retorts, the heavy vapours escape at once undiluted by the fire-resisting gases which are set free afterwards, and the heavy gases are thus exposed to the white heat of the upper part of the retort. If, however, according to the proposal of Vivian B. Lewes, producer-gas is introduced into the gas retort, such a dilution takes place at once which will produce a smaller quantity of tar, which is, however, richer in oils.

Börnstein has also worked on the formation of tar from coal at comparatively low temperatures (*Chem. Zeit.*, 1904, 927; *Z. Elektrochem.*, 1904, 1863; *J. Gasbeleucht.*, vol. 49, pp. 627, 648, 667; *Ber.*, 1906, 1238). When coal is slowly heated up to 450° C., neither aromatic hydrocarbons nor phenols are formed, but methane homologues and pyrocatechine. In that case coals from more recent strata yield tars below the specific gravity of water, older coals tars heavier than water. The gas produced at the same time contains but little free hydrogen, most of which is formed at higher temperatures by the decomposition of methane homologues and the formation of aromatic hydro-

carbons. The tar produced below 450° from coal contains some of the higher ("hard") paraffins; also isomethylanthracene and a hydrocarbon corresponding to "cracken," $C_{24}H_{18}$.

Even when the distillation of coal is carried out at higher temperatures for the purpose of making ordinary coal-gas, the composition of the tar may vary very much according to the *shape of the retorts* used, which causes the vapours to have more or less action on the hot material of the retort. This is proved by experiments made with Bueb's vertical retorts, which have attracted a great deal of attention during the last few years (Ger. P. 167367; *J. Gasbeleucht.*, 1905, 833; 1906, 259, 325; *Z. Verein. deutsch. Ingen.* 1906, 198). At Warsaw, where Bueb retorts were working alongside of the ordinary horizontal retorts, the same coal yielded quite different tars with both, as shown here:—

	Vertical retorts.	Horizontal retorts.
Specific gravity of tar, about	1·1	1·2
Free carbon	2 to 4 %	about 20 %
Water	2·17	3·5
Light oil	5·85	3·10
Middle oil	12·32	7·68
Heavy oil	11·95	10·15
Anthracene oil	15·96	11·64
Pitch	49·75	62·00
Loss	2·00	2·03

The tar from vertical retorts contains almost 50 per cent. less naphthalene than that from horizontal retorts.

Hayes (Silliman's *Amer. J.*, March 1859) had long before this made corresponding observations on the quality of the tar respecting the influence of the shape of the gas retorts. Where the volatile products are carried away from the hottest place through a narrow pipe, much less heavy and more light oil are obtained, and the coke is more compact and harder.

These differences are evidently connected with variations of the *pressure* within the retort. At a higher pressure the gas cannot escape so quickly, and remains a longer time in contact with the hot walls of the retort, which produces secondary decomposition, as proved by the carbon secreted on the retort-walls and in the liquid distillates. This fault is corrected by the employment of exhausters (*cf.* p. 31).

As a matter of course, the *difference of the quality* of the

coal used in gas-making (we here speak only of real coal, not of browncoal, etc., already referred to on page 19), influences the composition of the tar. Newcastle coals furnish tar rich in naphthalene and anthracene. Among German coals, that from Silesia furnishes much better tar than that from Westphalia. According to Deville (*J. Gasbeleucht.*, 1889, 693), the percentage of oxygen in the coal has great influence in that respect. According to the variations of that constituent, he distinguishes the five following groups :—

	I.	II.	III.	IV.	V.
	5 to 6·5 % Oxygen.	6·5 to 7 % O.	7·5 to 9 % O.	9 to 11 % O.	11 to 13 % O.
					Per cent.
Yield of tar . . .	3·90	4·65	5·08	5·48	5·59
„ water . . .	4·58	5·86	6·80	8·6	7·86
					Grams per cbm.
„ benzol in 1 cbm. of gas . .	26·67	37·02	35·96	38·94	33·02

It is especially injurious to the quality of the tar if the lighting-power of the gas is augmented by addition of *boghead* or any similar *bituminous shales* to the coal. In such a case, even at the highest practical temperature, hydrocarbons of the paraffin series appear more extensively in the tar. The benzol will contain hydrocarbons similar to petroleum-spirit, and the anthracene paraffin, neither of which impurities can be removed by the methods usually practised, viz., fractional distillation or crystallization. Hence many tar-distillers stipulate in their contracts that the gas-works must not mix more than 5 per cent. of shale (boghead, etc.), with their gas-coal.

Besides paraffins, boghead tar contains principally toluene and naphthalene, and but little benzene and anthracene. The real boghead, or Torbane-hill mineral, is now practically exhausted; but the name is still used in commerce for shales of much inferior quality. The shale-spirit got from these contains, along with the paraffins, very sensible quantities of benzene and toluene.[1]

Through the kind mediation of Professor Dittmar I have received the following information from Dr Ronalds on the tar

[1] Watson Smith, private communication.

from *cannel coals* and *boghead*. Scotch cannels were exclusively used in Edinburgh and Leith, and probably in most parts of Scotland, for making gas prior to the coal famine in 1851-53, when many companies took to using common splint coal, and some attempts were even made to use shale mixed with coal. Shales give little or no tar; and the naphtha (if *any*) is similar to that from boghead (the hydride series). The quality of the tar now made from the various kinds of cannel coal (such as those from Lesmahagow, Marquis of Lothian, Arniston, Benhar, Wallyford, and numerous other localities) is very different from that obtained formerly. Formerly, when *low* heats were used at the gas-works, as much as 8 per cent. of naphtha (*i.e.* benzene and its homologues) was obtained by distillation with steam. This diminished slowly as the heat employed at the gas-works increased, until it had fallen to about 3 per cent. The naphtha from Scotch tar was always rich in toluene, and contained less benzene than that from ordinary bituminous coal. It contains little naphthalene and very little anthracene—so little of the latter that its extraction is not worth while. It also contains considerable quantities of paraffins, but mostly of low melting-points. Naphthalene and paraffin seem to go together; wherever there is much of the one, the other is almost always present too.

Dr Kraemer (priv. comm.) regards the notion that solid paraffin occurs in real coal-tar as erroneous. In his opinion, solid paraffin only appears whenever cannel coal, or shale, or similar substances have been employed along with real coal; and the reason why naphthalene and paraffins generally occur together is simply this, that coals yielding much naphthalene usually require an addition of the above-mentioned substances in order to produce good gas. (It should be noticed that the different experience of Dr Ronald had been gained with another material, viz., Scotch cannel coals.)

When shale or boghead or similar semicoals are mixed with cannel or bituminous coal, the light naphtha is a mixture of the benzene and of the methane series; as these are very difficult to separate, the benzol is comparatively valueless as a commercial product. The heat used in the making of the gas and tar appears to have quite as much, if not more, to do with the quality of the products as the quality of the coal has.

A special investigation by Dr Bunte[1] shows the influence of the quality of coal on the quality and quantity of gas, tar, and ammonia produced in distillation. We extract from it the following statements (partly translated into English measures). The five descriptions of coals distilled had the following composition :—

Description of Coal.	Total contents of the Coal.					Composition of the organic substance.		
	C.	H.	O. (+N & S).	Water.	Ash.	C.	H.	O. (+N & S).
Westphalian (Consolidation) .	78·94	5·22	7·59	1·64	6·62	86·04	5·69	8·27
Saar (Heinitz I.) .	77·18	4·97	9·27	2·00	6·48	84·44	5·43	10·13
Bohemian (Thurn and Taxis) .	71·97	5·36	10·18	5·61	6·88	82·25	6·12	11·64
Saxon (Zwickau) .	68·75	4·91	11·05	7·79	7·50	81·16	5·80	13·04
Bohemian cannel coal (Pilsen) .	67·41	5·98	8·87	3·33	14·43	81·95	7·27	10·78

These coals, when distilled in an ordinary gas-retort, fitted up with special condensing-apparatus for experimental purposes, but otherwise working under normal manufacturing conditions, yielded for each 100 kg. of coal the following products :—

Description.	Coke, kil.	Gas.				Temperature of retorts, °C.	Tar, kil.	Ammon. liquid, kil.	Loss, kil.
		Kil.	Cubic metres.	Cubic feet per ton.	Illum. power candle.				
Westphalia	71·4	16·95	30·33	11,899	11·15	1360-1385	4·09	4·44	3·12
Saar . . .	68·3	17·71	30·18	11,835	10·27	1205-1290	5·33	6·90	1·76
Bohemia .	63·3	18·52	28·47	10,221	10·20	1240-1350	5·79	9·06	3·33
Zwickau .	62·7	15·81	25·46	9,140	10·59	1180-1240	5·22	11·89	4·38
Boh. cannel	56·3	25·72	30·38	11,916	18·17	1180-1350	8·81	6·45	2·72

This seems to show that the quantity of tar increases with the percentage of oxygen in the coal, apart from the necessarily different case of cannel coal. The increase of the yield of ammoniacal liquor is in the same direction; but this proves nothing, as neither the strength of the liquor nor the original percentage of nitrogen in the coal is stated.

[1] *J. Gasbeleucht.*, 1886.

Bunte's results have been completely confirmed by the report of the 1012 trials made, on a working scale, by the Paris Gas Company from 1874 to 1884, with 59 different classes of coal.[1] The conclusions arrived at are:—"The higher the percentage of oxygen, the more tar and ammonia is formed and the more hygroscopic water is contained in the raw coal; on the other hand, the yield of coke and gas is less with a rise in the percentage of oxygen."

American coal-tars are stated by White and Hess (*J. Soc. Chem. Ind.*, 1900, 509) to be inferior to European tar as regards the recovery of benzol, etc., but they are rich in anthracene. They give a number of analyses.

An interesting paper has been published by Porter and Ovitz (*J. Amer. Chem. Soc.*, 1908, pp. 1486 *et seq.*) on the "Nature of the Volatile Matter of Coal," as evolved under varying conditions. As the contents of that paper do not bear in any direct way on the matter treated in this book, we must confine ourselves to drawing attention to it.

Peters (*J. Gasbeleucht.*, 1908, p. 1114) also discusses the processes going on in the coking of coal.

The total yield of tar from the coal may be set down on the average as 5 per cent. on the weight. Wanklyn (*Gas Engineer's Chemical Manual*, p. 5) states that one ton of coking-coal (Newcastle coal) yields:—

	Lbs.	Per cent.
10,000 cubic feet of gas . .	380	17·0
10 gallons of tar . . .	115	5·1
Virgin gas-liquor* . .	177	7·9
Coke	1568	70·0
	2240	100·0

* That is, the liquor condensing from the gas alone without any water running down within the scrubbers.

Exact figures concerning the yield of tar in London and provincial gas-works have been given on pp. 21 and 22. According to Wurtz,[2] St Etienne coal only yields 4 per cent. of poor tar, but Anzin and Mons coal 6·73 per cent., and "Prussian" coal up to 7 per cent., of rich tar. Of the German coals, those from

[1] *J. de l'éclairage au Gaz*, juillet, 1886.
[2] *Dictionn. de Chimie*, i., p. 1631.

Upper Silesia yield the best, those from Westphalia the poorest tar. The yield of tar is given in the following table,[1] which shows that from various descriptions of coal, along with that of other products, on the average there is obtained :—

	Tar.	Ammoniacal liquor.
From coal generally .	4 to 6	6 to 10 per cent.
„ English coals .	4·5	6 „
„ Silesian „ .	5 to 6	9 „

1 ton (2240 lb.).	Gas.		Coke.	Tar.	Gas-liquor.	Loss.
	Cub. ft.	Lb.	Lb.	Lb.	Lb.	Lb.
Boghead cannel . .	13334	...	715	733·3	...	...
Newcastle . . .	9833	...	1426	98·3	60	...
Wigan cannel . . .	10850	...	1332	218·3	161·6	...
Lochgelly . . .	8331	...	1245	225	340	...
⅞ Lochgelly + ⅛ Boghead	9055	...	1200	400	170	...
$\frac{9}{10}$ „ + $\frac{1}{10}$ „ .	9050	...	1205	335	290	...
$\frac{11}{12}$ „ + $\frac{1}{12}$ „ .	9750	...	1240	227	270	...
Pelton Main (Durham) .	9500	...	1542	112·5	112·5	...
¾ „ + ¼ Boghead	12800	...	1366	206·6	116·6	...
Lesmahagow cannel, I. .	11681	461	1091	594	4·5	87·5
„ „ II. .	9878	483·5	1064	603	4·5	85
Ramsay's N'castle cannel	9016	410	1435	295	6·7	93·3
Derbyshire deep-seam .	9400	300	1335	219	179	207
Wemyss cannel, I. . .	10976	551	1124·5	224	...	340
„ „ II. . .	10192	528	1188	197	...	327
Wigan cannel . . .	9408	338	1326	250	...	326

Bunte (*J. Gasbeleucht.*, 1886, p. 595) obtained the following results with different coals :—

	Tar per cent.	Ammonia-liquor per cent.	Total per cent.
Westphalian coal . . .	4·09	4·44	8·53
Saar coal	5·33	6·90	12·23
Bohemian black coal . .	5·79	9·06	14·85
Zwickau coal . . .	5·22	11·89	17·11
Pilsen shale (Plattenkohle) .	8·81	6·45	15·26

The following statements (Muspratt-Stohmann's *Chemie*, 4th ed., v., p. 319) summarize the results obtained at 67 German gas-

[1] Stohmann-Kerl's *Chemie*, 3rd ed., p. 624.

works in 1891-92, working with gas-coal proper, without additions of boghead, etc. :—

100 kg. Coals yield :—	Gas, cubic metres.	Coke, kilog.	Tar, kilog.
Westphalian coal . .	24·8-31·9	59·1-76·0	3·4-5·5
	28·6	66·0	4·4
Saar coal	26·1-31·3	60·0-71·0	4·8-6·9
	29·5	64·9	5·9
Silesian coal . . .	24·9-31·2	59·5-74·1	3·8-6·0
	28·3	65·9	4·9
Zwickau coal	26·4-29·5	54·2-57·6	4·7-6·3
	27·64	55·3	5·6
English coal . . .	26·4-30·8	64·7-73·1	4·0-5·9
	28·6	68·5	4·8

Methods for determining the yield of tar from coal in the laboratory will be described at the close of this chapter.

Proposals for Increasing the Quantity or Improving the Quality of Tar in the Manufacture of Coal-gas.

We have already seen that both the quantity and the quality of tar differ with the quality of the coal and the temperature of distilling it, no doubt also with the pressure existing in the retort and the velocity with which the gases are evolved and are made to escape from the retorts. All these conditions, however, must in the first instance be made subservient to the aims of manufacturing illuminating-gas ; that is, obtaining the best yield and the best quality of gas, the tar being left to take its chance. Still it may be possible to introduce such improvements as will serve the purpose of improving the yield or the quality of the tar, and the following proposals have been made with this object :—

H. Aitken (B. P. 4644, 1883) considers that the large amount of water contained in certain kinds of coal, shale, and lignite (real coal does not contain much water) causes the coke to be too porous and light, and carries off much of it in the unburnt state. He therefore dries the coal in a tower by drawing or blowing heated air or hot products of combustion through it.

The coal thus treated is stated to yield much closer and heavier coke, a higher yield of gas, and tar containing more benzene. [Although this process might do for very moist materials, it would certainly not pay in most ordinary cases.]

N. A. Hélouis, of Paris, evidently inspired by the reading of Berthelot's and other great savants' researches, but without much regard to the conditions and requirements of practical work, obtained provisional protection (B. P. 5142, 1883) for a process based on the "rational and permanent production of acetylene." This is to be attained: 1. by a fixed temperature never exceeding a dull red-heat in the retorts [!]; 2. by the permanent action of a current of previously superheated gas and steam led into the retorts during the whole time of the distillation; 3. by maintaining a mean pressure of $\frac{1}{5}$ atmosphere in the retorts. Thus acetylene, the [hypothetical] generator of benzene, is to be permanently produced, whilst the benzene itself is protected against being condensed into more complex carburets, constituting heavy oils of less commercial value.

Heusser (Ger. P. 24728) also from purely theoretical considerations on the "condensing" action of acids, zinc chloride, etc., believes it possible to obtain at will hydrocarbons of a lower boiling-point by passing chlorine gas and hydrochloric-acid vapour into the gas-retorts; and hydrocarbons of a higher boiling-point by mixing the coal with zinc chloride, with or without the admixture of tar or tar-oils, and also passing hydrochloric-acid vapour into the retorts during the dry distillation. It does not seem necessary to criticise this process.

Byrom, Wigan, and Bennett (B. P. 3736, 1884) propose removing the various products of distillation from the retorts before they are mixed, thus avoiding the expense of redistillation. This is to be done by providing the retort with a number of openings along its highest part, each exit-pipe being supplied with a bend which may be inclined downwards, the pipe being of sufficient length to secure the condensation of the liquid, the gases to be drawn off by an exhauster. This process, if at all feasible, would evidently apply more to the distillation of shale, etc., for paraffin oil than to that of coal for gas-making.

Kunath (*Chem. Zeit.*, 1885, p. 1893) attributes the thickening of tar not merely to the presence of particles of coal carried over mechanically with the gas, but principally to a local

superheating of the gas. Thinner tar is to be obtained by charging the retorts with as much coal as possible, and thus reducing the gas-space and the contact surfaces.

J. Young (B. P. 14840, 1886) mixes the coal before carbonizing with common salt in proportions varying with the composition of the coal, usually 4 lb. per ton of coal, in order to improve the quality of the coke, to facilitate the purification of the gas, and to increase the yield of gas, tar, and ammonia.

Dvorkovich (*J. Soc. Chem. Ind.*, 1893, p. 403) considers the present way of manufacturing gas as irrational. The coal is better carbonized at a low temperature in the presence of an inert gas (carbon monoxide or hydrogen); in this case a large quantity of "coal-oil" passes over, similar to petroleum residues, which is to be split up by overheating into more gas and aromatic hydrocarbons, as effected by Letny and Ragosine (see below).

We shall later on meet with several other attempts at improving the quality of the tar or increasing the quantity of its more valuable constituents by a special treatment while in the gas-retorts or subsequently.

Recent patents for improvements in the recovery of tar in the process of gas-making:—

Smith and Albright (B. P. 9070, 1902).

Holmes (B. P. 20677, 1903).

Planting (Ger. P., appl. P13626).

Everitt (B. P. 13316, 1904).

Several inventors employ *steam*, either in the retorts or upon the gas after leaving them, for the purpose of facilitating the precipitation of the tar (and some ammonia) on cooling. Thenius recommended this many years ago (Wagner's *Jahresber.*, 1865, p. 738). Recent patents on this line:—

Heinemann (Ger. P. 138250).

Burgemeister (Ger. P. 154028).

Th. von Bauer (Ger. P., appl. B36982) for coke-ovens.

Recovery of the Tar suspended in the Gas.

Ordinary coal-gas always contains a good many tarry particles in mechanical suspension. These particles are to some extent precipitated in the gas-pipes, and are found both

at the gas-works and in the "siphons" (traps) of the street pipes as oils or as masses of crystallized naphthalene. These oils have been examined in detail by Gasch.[1] He found that they gave off—

3 to 6	per cent.	up to	100°,	
5 „ 8	„	from	100°	to 180°,
5 „ 15	„	„	130°	„ 150°,
19 „ 36	„	„	150°	„ 180°;

on the whole, 47 to 76 per cent. up to the points where naphthalene appeared. They contain numerous sulphur compounds—below 100° carbon bisulphide, above 100° probably thiophene. An exact examination of these oils (which do not appear to be systematically collected anywhere) is still wanting.

The quantity of tar can be considerably increased by supplementing the condensing-action of the air-condensers and scrubbers by more efficient apparatus. This is the object of the process of Pelouze and Audouin,[2] which is being worked very successfully at Paris and elsewhere. That they are not the real inventors of the process has been decisively proved by Colladon.[3] The invention proceeds from the principle that mere cooling cannot possibly condense all the tar, because the latter remains mechanically suspended in the gas in the shape of extremely minute liquid drops, *i.e.*, in the form of a mist. A portion of this is retained in the coke-scrubbers, but very far from all of it. The result is different when the gas is made to issue through narrow apertures and impinge against a broad solid surface, over which it must spread. The fine liquid particles are thus brought into very much increased contact with each other and with solid bodies, gather into larger drops, and are thus retained. Fig. 2 shows how this principle is carried out. The gas passes into a vessel A through the inlet-pipe B, and leaves it at C. Inside A is a cylinder D, the proper purifying-apparatus, which floats in the hydraulic tar-lute E, so that the gas can only get from B to C through the perforated sides of D. The latter are made of three concentric sheets of brass, $\frac{1}{16}$ inch apart, and perforated with many holes. The holes *a a* (Fig. 3) are $\frac{1}{16}$ inch wide, arranged in

[1] *J. Gasbeleucht.*, 1873, p. 65; Wagner's *Jahresber.*, 1873, p. 914.
[2] *Comptes rend.*, lxxvi., pp. 264, 928. [3] *Ibid.*, lxxvii., p. 819.

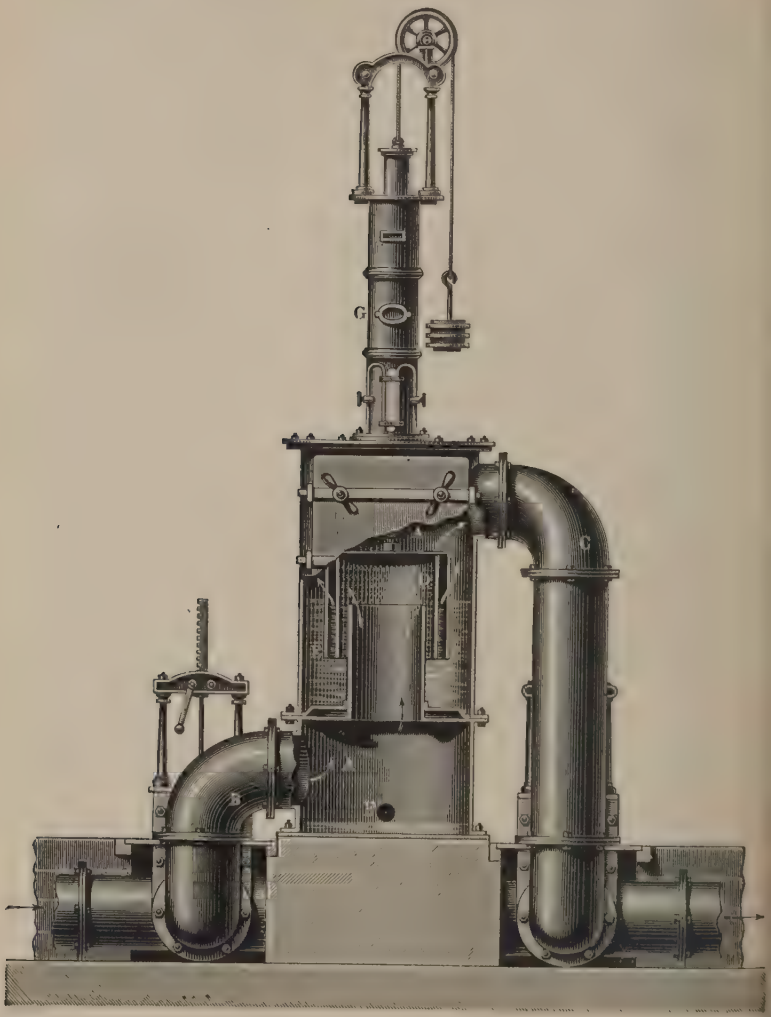


FIG. 2.

three rows placed transverse to each other, so that the jets of gas, issuing through the holes of the innermost plate, meet with the solid portion of the middle plate, and when issuing through the holes of the latter again meet solid portions of the outermost plate, from which at last they can get into the upper space of B. Since experience has shown that the holes of the middle plate especially are readily clogged up with tar, the apertures of this plate are now made (as shown in Fig. 3) larger and square. It

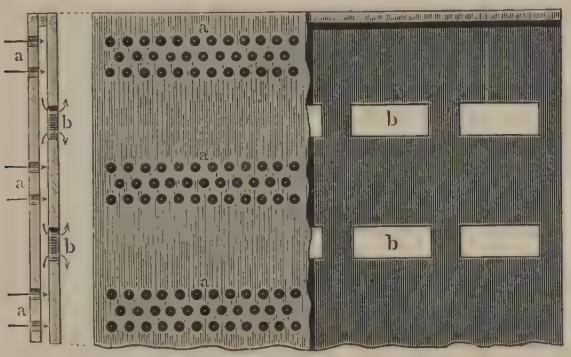


FIG. 3.

has also been attempted to replace the holes by vertical slits, which do not so easily get stopped up. The tar condensed by the impact on the plates runs into the tar-cistern E, flows over and runs away at F. Since of course some pressure is lost in this apparatus, it is necessary to let the gas, previously well cooled, issue under a certain surplus pressure, say $1\frac{3}{4}$ to $1\frac{7}{8}$ inch, which is kept constant by the automatic regulator G.

In 1876 there were eight such condensers at work in Paris, which produced:—At the Ternes works, from each 1000 cbm. of well-cooled gas, 9 kg. of tar; at the La Villette works, from 1000 cbm. of gas not so well cooled, as much as 72 kg. of tar, and 16 litres of liquor containing 80 g. of ammonia per litre. The tar is much lighter than ordinary gas-tar; it yields 20 per cent. of light oils, instead of 3 to 5 per cent.

This apparatus is employed at many French gas-works, and it has also been introduced into other countries, for instance, into Germany. At first the objection was made to it that it is

very difficult to keep the holes from being clogged up, and that it is doubtful whether the extra yield of tar is not counterbalanced by the loss in the illuminating-power of the gas. But as a matter of fact, the apparatus has been in full work at quite a number of gas-works outside of France up to the present time, and during the last few years it has also been introduced in quite a number of Westphalian coke-works for recovering the tar from coke-oven gas.

Other apparatus, on the same principle, has been patented by Fr. Lux (Ger. P. 40897) and Servier (*J. Gasbeleucht.*, 1880, p. 639). The same object, together with scrubbing the gas by water, is pursued by the inventions of Chevalet (*J. Gasbeleucht.*, 1883, p. 420), Fleischhauer (*ibid.*, 1887, pp. 27 and 1020), and Schumann & Küchler (Ger. P. 67767); also by Drory's tar-scrubber, perhaps that apparatus which is most employed at the present time and by which upwards of 90 per cent. (sometimes 99 per cent.) of the tar and 20 per cent. of the ammonia is taken out of the gas. Some of the most recent proposals for separating the liquid and solid from the gaseous part of the mixture are the following:—

Scheibe (Ger. P. 184038) employs a fan-blast; by the impact of the gas against the outer shell, the liquid (and solid) particles are made to adhere to this, until they flow downwards, where they are constantly removed.

The Gasmotorenfabrik Deutz (Ger. P. 183823) employs a number of chambers superposed over one another, with impact surfaces inside, the shock against which causes the precipitation of the tar.

The Berlin-Anhaltische Maschinenbau Aktien Gesellschaft (Ger. P. 183413) employs revolving drums, placed in superposed chambers, with brushes in the intermediate space. The drums dip into the dish-shaped bottoms of the chambers.

Ott (Ger. P. 183519) also employs a system of superposed chambers, with impact surfaces.

Recovery of Benzol contained as Vapour in Coal-gas.

It has long been known that a good deal of benzol (as we will call benzene and its homologues in this connection) is contained in coal-gas, and adds much to its illuminating-power.

According to the extensive experiments made by the Paris Gas Company (*supra*, p. 28), the percentage is pretty constant in the case of the various descriptions of coal, and amounts for 1 cbm. of gas to 30 g. of benzene and 9 g. of toluene, etc.; by volume to 1·05 per cent., along with 5·5 to 4·8 per cent. by volume of heavy hydrocarbons belonging to the fatty series. The benzene, etc., separates in the liquid state when cooling down the gas to −70° C., whilst the other heavy hydrocarbons remain in the gaseous state. From this we may make the following calculation:—One ton of coals yields about 11,000 cub. ft., or, say, 300 cbm. of gas, containing 11·7 kg. of benzol, etc. At the same time about 1 cwt. of tar is formed, from which about 0·5 kg. of benzol is obtained. *Hence coal-gas in this case contained 23 times as much benzol as the tar formed from the coal at the same time;* and this is a very legitimate stimulus for attempts to recover benzol from coal-gas.

St Claire-Deville (*J. d. Us. à Gaz*, 1889), by cooling down the gas to −70° C., obtained from 1 cbm. of Paris gas 35·48 g. of aromatic hydrocarbons, containing:—

Benzene, boiling-point 81°	73·13	per cent.
Toluene, „ 111°	13·00	„
Xylene and higher homologues, boiling-point 139°	8·75	„
Residue and loss	5·12	„

In Bunte's investigation at the Karlsruhe gas-works (*J. Gasbeleucht.*, 1894, p. 601), 100 kg. of coals yielded:—

1. 30·0 cbm. = 17·04 kg. of gas, containing 938 g. benzene (95 per cent. of the total C_6H_6), and 312 g. toluene (89 per cent. of the total C_7H_8), with traces of naphthalene.
2. 5 kg. of tar, containing 5 g. benzene (= 5 per cent.), 40 g. toluene (= 11 per cent. of the total C_7H_8), 300 g. naphthalene, 70 g. phenol, 20 g. anthracene.
3. 11 kg. ammoniacal liquor.

Further investigations by Bunsen (*Gasometr. Methoden*, 1877), Berthelot (*J. Gasbeleucht.*, 1876, p. 409; 1877, p. 525), Knublauch (*ibid.*, 1880, p. 256), Dennstedt and Ahrens (*Berl. Ber.*, 1894, p. 601), whilst confirming the large proportion of benzene and toluene contained in the gas in the state of vapour, do not make it out quite as high as the first Paris investigation. As final result we may state that *there is about 15 times as much*

benzene and toluene vapour in the gas compared with their percentage in the tar.

The percentage of benzol in *coke-oven gases* is decidedly smaller than in ordinary coal-gas made for illuminating purposes (which can be easily understood, since the quality of coal used for coke differs from that used for illuminating-gas). Kraemer (*Glückauf.*, 1897, p. 381) estimates the quantity in coke-oven gas = ½ of that in illuminating-gas. In 1900 the Westphalian factories obtained an average yield of 0·4 per cent. benzene and 0·09 per cent. toluene on the coal coked, the Laar works averaged 0·9 to 1 per cent. (Haarmann, p. 28).

S. Mellor (B. P. 5604, 1882) proposes to obtain benzol, toluol, or their homologues by *subjecting coal-gas to a pressure of 4 or more atmospheres*, whereby those hydrocarbons are to be deposited in a liquid form. This proposal is manifestly impracticable, if it is intended to be applied to ordinary coal-gas. But it seems a different matter when we consider the "rich" gas obtained from petroleum, fatty oils, etc., and subjected to several atmospheric pressures, in order to light railway-carriages and the like. In this case liquids are spontaneously condensed, and it needs only to be called to mind that Faraday, in 1825, discovered benzene in a liquid condensing from compressed oil-gas. Greville Williams (B. P. 4663, 1884) treats such liquids in the following manner:—They are distilled, and all coming over below 65°·5 is rejected. The second portion is collected between 65°·5 and 87°·5, the third portion above 87°·5. To separate benzene (toluene, etc.) from these distillates, they are subjected to the action of dilute nitric acid (100 gall. requires 50 gall. commercial nitric acid and 50 gall. water), or of a mixture of sodium nitrate and sulphuric acid (190 lb. commercial nitrate of soda, 218 lb. commercial oil of vitriol, and 24½ gall. water to 100 gall. oil). The mixture is then distilled in a salt-glazed stoneware still by means of a steam- or water-bath; benzene and its homologues readily come over, the homologues of olefiant gas being converted into compounds, which remain behind in the still. The scientific principles underlying this proposal have been discussed by Greville Williams in the *Chemical News*, vol. xlix., p. 197. He found that the liquid obtained in manufacturing the "Pintsch gas" contained from 65·6 down to 24·6 per cent. of benzene and toluene, according to its specific gravity,

which varied from 0·850 to 0·760. It should be noted that any process involving the distillation of liquids containing a large quantity of free nitric acid, and then necessitating the use of stoneware stills, must present a good deal of inconvenience.

Armstrong[1] has also subjected to examination the liquids condensing from Pintsch gas and some other descriptions of compressed gas made from oil or petroleum. These liquids, commonly called "hydrocarbon," are practically free from paraffins; they essentially consist of benzene and toluene (rarely less than 50 per cent.), of the dimethyl- and trimethyl-benzenes occurring in coal-tar, of napthalene, of the hydrocarbons of the olefine and "pseudo-olefine" series (viz., ethylene, propylene, amylene, hexylene, and heptylene), and the "pseudo-acetylene" series (especially crotonylene, dimethylene-ethane, and isoallyl-ethylene); also much cyclopentadiene. This "hydrocarbon," amounting to rather less than 1 gall. per 1000 ft. of compressed gas, is not used by tar-distillers, as it is too difficult to separate the benzene and toluene from the other hydrocarbons; it is exported to Belgium, where it is said to be used for varnish-making. Entirely different from this liquid is the "tar" depositing from the oil-gas prior to its collection in the gas-holder, and amounting to about 5 gall. per 1000 ft. of gas; it contains neither acids nor basic constituents, and little, or even hardly any, benzenoid hydrocarbons, but mostly undecomposed petroleum hydrocarbons—that is, the material started from.

Etard and Lambert (*Comptes rend.*, cxii., p. 495) have examined the liquid condensed by compressing the rich gas made from paraffin oil, and have found therein 60 per cent. benzene, 10 per cent. toluene, 6 per cent. non-saturated light, and 10 per cent. ditto heavy hydrocarbons, boiling between 140° and 190°; moreover a hydrocarbon of the formula C_5H_6, boiling at 42°·5, easily polymerized in the cold, which they call "pyropentylene," and which is probably identical with the "cyclopentadiene" discovered by Kraemer and Spilker also in ordinary coal-tar (*Berl. Ber.*, 1896, p. 533).

According to Kraemer (priv. comm.), it is easy to separate the benzenoid hydrocarbons from the olefins by means of *free*

[1] *J. Soc. Chem. Ind.*, 1884, p. 462; Armstrong and Miller, *J. Chem. Soc.*, vol. xlix., p. 74.

chlorine, which fixes the latter, so that benzol, etc., can be blown off. This process has been carried out in practice; but it is now supplanted by a still better one, consisting in a treatment with picric acid.

Cooling to a low temperature has also been proposed for the purpose of condensing hydrocarbons from coal-gas; but the objections to be made to this operation, if intended to apply to ordinary coal-gas, are quite obvious.

A second series of proposals refers to depriving either ordinary or specially prepared coal-gas of the particles of aromatic hydrocarbons suspended and contained as vapour in it, by *passing the gas through liquid absorbents* for those substances. Many years ago A. Vogel[1] passed the gas through colza-oil, which increased 20·5 per cent. in weight and very much in illuminating-power, whilst that of the gas did not suffer. The last statement is more than doubtful; it is now generally assumed that the illuminating-power of coal-gas is to a very great extent due to the presence of benzene vapours, the results of Berthelot[2] in this direction having been confirmed by many subsequent investigations of Frankland and other chemists. On the contrary, by removing the benzol from coal-gas, it becomes a "poor gas," unfit for illuminating purposes, unless "carburetted" again in some other way, *e.g.*, by the vapours from petroleum-spirit and the like, or else applied (as it had been already previously done with water-gas) on the principle of the "incandescent" light, namely by introducing some solid body, as platinum, magnesia, zirconium, etc., into the flame in order to give out light after having been raised to a white heat. That the light-giving constituents of coal-gas are almost entirely removed by passing it through heavy mineral oils was noticed in 1868 by Cusiter; but his observations were only made known to a very limited circle in 1874.[3]

Whilst Vogel evidently did not aim at extracting benzol as such, this was the aim of a process devised by Caro, A. Clemm, K. Clemm, and Engelhorn (B. P. dated Feb. 17, 1869), during a period in which the price of benzol had risen enormously. They brought the gas into contact with oils of high boiling-points, such as petroleum, paraffin oil, or fatty oils, and separated the

[1] *Dingl. J.*, vol. cliii., p. 464. [2] *Comptes rend.*, vol. lxxxiv., p. 571.
[3] Davis, *J. Soc. Chem. Ind.*, 1884, p. 432.

benzene and toluene absorbed by subsequent fractional distillation, so that the residual oil could be used over again as an absorbent. This process did not hold its ground for any length of time, the decline in the price of benzol and the reduction in the value of the gas making it unremunerative.

In 1875 J. Barrow patented the application of artificial refrigeration to the collection of the vapours of solvent naphtha evolved in the working of indiarubber, afterwards absorbing them in oil—an idea which has since been utilized for a similar treatment of the benzene vapours contained in coal-gas.

In 1882 Caro's idea was once more taken up, first by J. Hardman (B. P. 4312, 1882), who began the process in the gas-retort itself, distilling at a very high temperature in order to produce more benzene and its homologues. These hydrocarbons are separated from the gas by means of condensing-apparatus, which are charged with anthracene oil or other heavy hydrocarbons. The gas, after this treatment, is rendered useless for illuminating, and is only fit for heating purposes. We here meet with the idea that the manufacture of gas is to be treated as a secondary process, that of benzol being the primary object in view, to be promoted by a special treatment of coal.

A very similar course was taken by G. E. Davis (B. P. 5717, 1882; and 4468, 1883). He proposed ascertaining by experiment, for each particular kind of coal, the minimum temperature at which it will yield the maximum quantity of benzol without forming paraffins. This would be a lower temperature than in ordinary gas-making, and only 7000 to 8000 cub. ft. of gas would be obtained from each ton of coal. Before charging into the retorts, the coal is to be moistened with some of the concentrated spent ammonia-water containing the sulphocyanides, so that the temperature of the retort is lowered and more ammonia is obtained. The gas is then washed or scrubbed with water, previously warmed to diminish its power of dissolving hydrocarbons and hydrogen sulphide. It is then passed through a weak acid or other substance capable of retaining the ammonia, and is then purified, as usual in gas-works, from cyanides, sulphocyanides, and a part of its hydrogen sulphide, leaving part of the latter purposely unabsorbed, as it is wanted afterwards. Now comes the operation interesting us most

here:—The gas is passed, at as low a temperature as possible (producing this by an air-cooling or freezing-machine, or else by the expansion of the gas after previously compressing it), through a hydrocarbon oil boiling at a high temperature. It then loses most of its illuminating-power, and is used as fuel for heating the retorts. In this process the H_2S previously left in is burned into SO_2. The products of combustion are brought into contact with ammonia-gas or ammonium carbonate, obtained by heating the ammoniacal liquor previously formed, whereby ammonium sulphite is produced, part of which is oxidized by the excess of air into sulphate. The inventor states that he thus obtained from 1 ton of coal, at a temperature of about 650° C., 16 gall. of tar, 37 gall. of ammoniacal water, 11 lb. of sulphur, 12½ cwt. coke, and 7000 cub. ft. of gas, which gave 4 gall. of benzol testing 90 per cent. at 100° C. The gas can then be used for heating (for instance) the retorts, or it can be used for lighting by means of some "carburetting" process.

A detailed description of Davis's process, and an analysis of the crude benzol obtained, is found in the *Journal of the Society of Chemical Industry*, 1883, p. 522. He admits there that the loss of absorbing oil is greater than at first anticipated, and that the process will only pay with benzol at a certain price, which was then easily obtainable (4s. to 5s., or at least 3s. per gallon), but which is out of the question at the present time. It is also evident that such a lowering of prices, if it had not occurred from other causes, would have been the inevitable consequence of any large extension of the process. In the discussion on Davis's paper it was stated that it takes all the gas produced, and 1 cwt. of coke in addition per ton of coal, to heat the gas-retorts.

E. Drew (B. P. 5039, 1883) proposed certain mechanical arrangements for treating the gas with heavy hydrocarbon oils. This patent has been made void; also another patent of the same inventor (No. 5505, 1883), in which it was proposed to treat the gas with such oils in a highly compressed state.

Levinstein (*J. Soc. Chem. Ind.*, 1883, p. 217) points out that the quantity of benzol to be extracted from coal by these processes (carbonizing it for that special purpose, and condensing the benzol from the gas by oily absorbents) is thirty

times the amount of that yielded by coal in the ordinary process, namely, allowing most of the benzol to remain in the gas, and only recovering what is found in the tar. The benzol obtained by the new processes, however, is not so easily nitrifiable as that made from tar.

While in the case of ordinary illuminating-gas it is a doubtful advantage to extract from it its most valuable light-giving constituent, benzene, and thus to greatly reduce its value, and while at the present time the carbonization of coal in such a way as to make the production of benzol the principal aim is utterly unremunerative, it seems a much more promising idea to submit the gases obtained *as a by-product in coke-making* to a similar treatment for extracting the benzol, instead of burning the latter as fuel for the coke-ovens, along with the great bulk of those gases. It is evident that in this case the benzol may be considered a clear profit; for the gases are always far more than sufficient for heating the coke-ovens even after abstracting the benzol. Although the great industry which has sprung up in that line does not apply to ordinary illuminating-gas, but to that of coke-oven gases, treated in the next section, we shall describe the apparatus used for that purpose in this place, since it is entirely on the same lines as that intended for taking the benzol out of retort-made illuminating gas.

The pioneer in this field was Carvès (B. P. 15920, 1884), who applied the process to the gases produced in his own coke-ovens (*cf.* later on.)[1] He employs as an absorbent for extracting the benzol from his waste gases the heavy portions of the oil that are obtained from the distillation of the tar procured from his own ovens. The gas is first made to pass through scrubbers consisting of upright cylinders, filled with pebbles or ganister, over which the oil is made to flow down. From the scrubber the gas passes into one or more wash-boxes, the lower compartment of which is again charged with heavy oil, and communicates with an upper compartment by means of a great number of small tubes passing down from the partition and dipping into the oil, so that the gases entering above are caused, by pressure or by exhaust at the exit of the

[1] A patent for the same idea has also been taken out by J. Coates (B. P. 11202, 1885).

lower compartment, to pass down these tubes and to bubble up through the liquid. Several of these wash-boxes are employed in combination, and are so arranged that the oil flows downward from the first to the second, and so on to the last one, while the gases first enter the lowest and successively pass on to the highest wash-box, and thence to the ovens to be burned. The oil coming from the lowest box is further made to feed the above-mentioned scrubber, so that the gases richest in light hydrocarbons come into contact with the oil that has already taken up most of the hydrocarbons from the preceding gas, and the almost exhausted gas is always brought into contact with fresh oil. In order to separate the benzol from the heavy oil, the mixture is heated in a still provided with an external steam-coil, or heated from without by a fire or by a coke-oven gas, to a point where the light oils are volatilized while the heavy oil is not affected. The escaping vapours are condensed in a worm in the usual manner; the heavy oil remaining behind is used over again in the wash-boxes and scrubber, as described above.

The process of Carvès does not seem to have been carried out on a real working scale in his own country. This was done first by Brunck (*Stahl u. Eisen*, 1892, p. 186) at Dortmund and by Hüssener at Gelsenkirchen. His process has been kept quite secret, but is evidently identical in principle with that of Carvès, and only differs from it in the shape of the apparatus. The absorbent used by him is prescribed to be solvent naphtha, consisting of pure coal-tar oil furnishing at least 90 per cent. distillate between 160° and 200° C., not secreting any naphthalene when cooled in ice-water, and containing only traces of phenol. By this process from 3 to 7 kg. of pure benzene is obtained from 1000 kg. of coal carbonized.

During the last twenty years a number of benzol-recovery plants have been erected in Germany on the lines laid down by Carvès. The coke-oven gas is first cooled down in the usual way, to condense most of the tar and part of the ammonia; the remainder of the ammonia is then removed by scrubbing with water, and the gases are then passed through similar scrubbers (*e.g.*, towers with many perforated shelves, the holes being luted by bell-covers), which are fed with heavy coal-tar oil.

Donath (*Fischer's Jahresber.*, 1894, p. 21) gives some details

on the above subject, from which we quote the following notes. The gas is forced through the absorbing columns by means of a blowing-engine, but first passes a collector and a cooler, to equalize the current and to remove the heat generated in compression. The columns are 7 ft. wide and 10 ft. high, and resemble those employed in ammonia-soda works, the gas entering from below. The absorbing-oil takes up at most 10 per cent. of its weight of benzol, sometimes only 6 or 7 per cent. All of this has to be heated to 200° C., in order to distil off the benzol. The coolers, connected with the stills, serve at the same time for a previous heating of the benzol-oil. The absorbing-oils can be used twenty times over again before they become too thick by the accumulation of naphthalene and tar, and must be removed. This loss amounts to about 5 per cent. per annum. The cost of plant for treating the gas from 300 tons of coke per day is £4300; the expense of working, inclusive of interest and amortization, is about £4350 per annum. The yield of benzol varies from 0·3 to 0·7 per cent. of the coal carbonized.

We owe the following details and diagrams to Dr H. Hirzel, Leipzig-Plagwitz. Fig. 4 shows a complete benzol-absorbing or "oil-washing" plant, according to Hirzel's German patent No. 99379, for treating from 3,500,000 to 5,200,000 cubic feet of coke-oven gas per 24 hours. There are three oil-washers of different construction, 8 to 10 feet wide and 16 to 23 feet high. A set of pipes, 18 to 20 inches wide, conveys the gas from below, at A, first into a Hirzel's tuyere-washer (Ger. P. 96228), into which the oil is forced through 200 up to 400 jets (*a*) in such manner that a spray is formed, filling the whole of the space, which quickly and completely removes the oil from the gas coming from the washer B. From here the gas travels through pipe C into a "bell-washer" (D), and passes through this also from the bottom upwards, being constantly brought into contact with the oil by means of the bells or caps *g*, dipping into the oil. The latter enters at the top at *d*, and descends from compartment to compartment. These washers are now made with 24 or more compartments, containing 3000 or 4000 bells. They act very well, but are more complicated and expensive than the tuyere-washers. Lastly, the gas enters through E into the "shelf-washer" F, which it leaves at the top at *f*. This contains

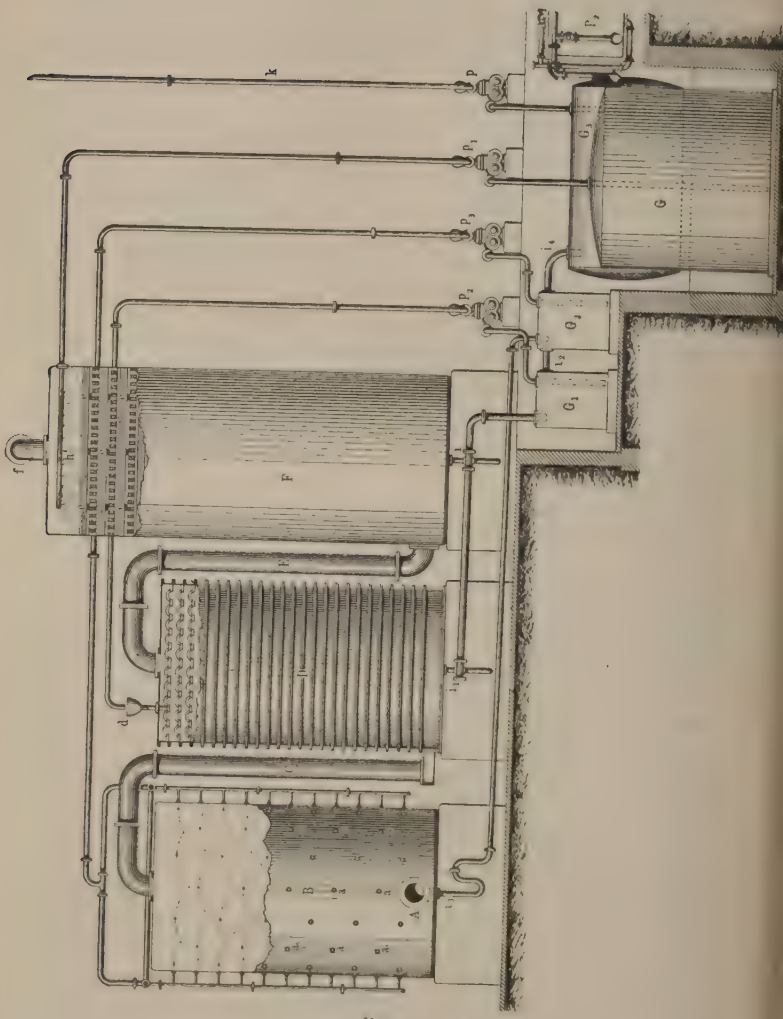


FIG. 4.

a number, say 28, of superposed wooden latticework or wirework shelves, on which the oil runs from the sprinkler *h*, passing through the interstices of the lattice shelves.

Whilst the current of the gas runs from A to B, D, F, and the exit at *f*, the washing-oil travels in the opposite direction. It is pumped from the store-tank G by pump p_1, first into the last washer F, where it meets almost debenzolized gas and takes the last benzol out of it; it flows through *i* into tank G_1, from this through pump p_2 into the bell-washer D and through i_1 back into G_1. The overflow from G_1 leads through i_2 into tank G_2; from here pump p_3 forces the oil into the tuyere-washer B, where it meets with fresh gas and is now run back through i_3 into G_2. The overflow of this tank leads through i_4 into the collecting tank G_3, from which the now enriched oil is pumped by pump *p* through pipe *k* into the stills (see below).

Some employ two different kinds of washing-oil, but Hirzel prefers using only one quality, which serves for taking 98 per cent. of all benzol out of the gas. The oil must be neither too thin (as it will then not remain long enough in contact with the gas) nor too thick (as it will then froth and solidify in the cold). The best oil shows the following property :—

Distilling off up to	240° C.,		6	per cent.
„ „	250	further	13	„
„ „	270	„	27	„
„ „	280	„	12	„
„ „	300	„	25	„
„ „	310	„	6	„
„ „	320	„	5	„
Solid residue	. .	.	6	„
			100	

Care should be taken that very little distils over 300° C.

It is also very important to employ the oil at the proper temperature. Already from 25° C. it loses some of its absorbing-capacity, and from 40° the latter is very slight. The best temperature is from 15° to 20°; an artificial cooling to 10° or below does not offer an advantage corresponding to the trouble.

From G_3 the oil is continuously pumped by *p* through *k* into the elevated store-tank H (Fig. 5), and is from here continuously fed into one or more Hirzel's stills, K. First the oil, conveyed

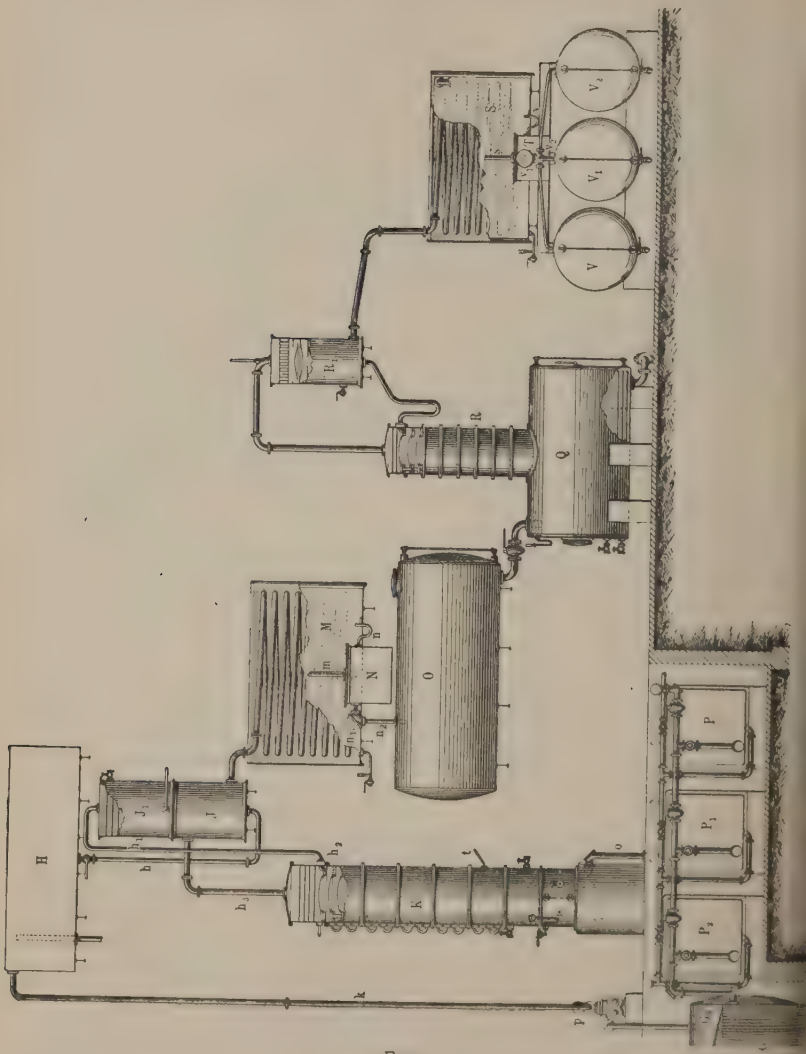


FIG. 5.

through pipe h, passes the heater J J_1 from the bottom upwards. The lower part, J, is heated by the vapours coming from column K ; the top part, J_1, is heated by direct steam. The warm oil leaves the heater at h_1, and through h_2 enters the column K near the top. This column is distinguished from others by steam-heating coils, placed in each chamber, covered by the oil, and heating this up to 110° or 115°. This is necessary to enable a slow current of dry steam to drive out the benzol. At the top, through h_3, steam and benzol vapours escape, pass through the lower part of the heater J, and from here enter the condenser M. From here the water and the crude benzol run into the separator N, with its vapour-pipe m ; and from this the water runs off by itself at n, the crude benzol (visibly) through n_1 and n_2 into tank O.

Such a column of 3 feet 3 inches diameter distils, in 24 hours, 60 cubic metres (about 2000 cubic feet) of saturated washing-oil at a pressure of 4 or 5, or even 3, atmospheres. If the temperature in the columns is properly regulated, by the aid of thermometer t, to stand at 115° C., the crude benzol collecting in O tests regularly 50 per cent., and is very little coloured. At 130° the vapours already contain part of the washing-oil, and at 150° to 160° this can be entirely brought over (see below).

The hot washing-oil, now free from benzol, leaves the column through o, runs into the cooler P, then through other coolers P_1, P_2, or more, and at last into tank G (shown also in Fig. 4). It is therefore in constant circulation.

The 50-per-cent. crude benzol from O is usually rectified for 90-per-cent. benzol. It is for this purpose run into the steam-still Q, with a column-top (R), a dephlegmator (R_1), and a condenser (S). From the latter we obtain "first runnings," then 90-per-cent. benzol and "last runnings" (toluol, etc.). These flow into the separator T, with vapour-pipe s ; the water alone runs off through v, the distillates (visibly) at v_1 ; the three-way cock v_1 directs them into either of the receivers V, V_1, or V_2. The 90-per-cent. benzol is perfectly colourless, limpid, and easily purified in the usual manner by washing with sulphuric acid and caustic-soda solution. The residue remaining in Q is collected by itself or mixed with the washing-oil.

If the temperature of 115° in the still is not exceeded, the washing-oil suffers no decomposition and very little of it is lost.

It might be used over and over again for ever, if the coke-oven gases coming from the condensers were free from tarry matters. But the condensers usually employed do not purify them sufficiently from naphthalene and tarry matters, which collect in the washing-oils and gradually diminish its absorbing-power. Spent oil sometimes contains 50 per cent. of naphthalene and pitch. Such oil must be regenerated, which can be done by distilling it in ordinary tar-stills; but this produces a washing-oil containing too much naphthalene and constituents boiling over 300°. It is much better to regenerate the spent washing-oil in a heatable Hirzel-column at 150° to 160° C., in which case the distillate consists essentially of oils boiling below 300° C., and, after separating the naphthalene by cooling, forms a most excellent absorbing-oil. The residue from the column is good soft pitch.

The above-described process had been carried out in 1900 with twelve large plants. Its advantages are: treating very large quantities of coke-oven gas in a limited space, distilling the washing-oil *continuously*, and obtaining at once 50 per cent., by a second distillation colourless 90-per-cent. benzol. The consumption of steam and cooling-water, owing to the low temperature, is comparatively small. The work is automatic, and one man can superintend the whole plant.

Marks (B. P. of the Compagnie pour la Fabrication des Compteurs et Matériels d'Usines, No. 10577, of 1897) employs for this purpose revolving drums, through which both the absorbing liquid and the gases travel in a circuitous way.

For washing out benzol from coal-gas or coke-oven gas, Heuss recommends a mixture of equal portions of creosote oil, containing not above 2 per cent. of naphthalene, and anthracene oil which yields no notable secretion of anthracene when cooled down to $-4°$ (private communication).

Heinzerling (B. P. 12390, of 1892) condenses benzol from the gases from shale and coke by means of cold, either directly or after removing the tar and ammonia. They are then compressed and cooled down to $+5°$ or 10° C., or passed direct into a solution of sodium or calcium chloride, kept at temperatures of $-10°$ down to $-45°$. Here most of the benzene is separated as a kind of grease on the surface. The escaping gases are

forced to yield the liquid drops carried along by passing them through sieves, and then enter into an expansion cylinder, where they are brought down to a plus-pressure of $\frac{1}{2}$ or $\frac{1}{4}$ atmosphere, utilizing the mechanical force thus generated to compress a further portion of fresh gas. The gas issuing from this cylinder is again deprived of liquid particles, and is used for a preliminary cooling of the above-mentioned saline solutions. The latter may be dispensed with by simply allowing the compressed and cooled gas to expand, which causes the benzol to separate out in consequence of the fall of temperature, and admits of cooling fresh compressed gas by the same means. This process was practically carried out at a Silesian works, to recover the benzol from 40,000 cubic metres gas per day. About 145 tons of crude benzol were actually obtained at a cost of 13s. per 100 kg. crude benzol, apart from interest and amortization. Owing to this, under most conditions excessive, cost and other circumstances, the process was stopped.

The Gewerkschaft König Ludwig (Ger. P. 136780) scrub the gases as usual with heavy coal-oil on the counter-current principle, and expel the volatile parts absorbed by means of steam, overheated to 300°, in which case all the naphthalene is also expelled, so that the absorbing-oil, after cooling, can serve over and over again.

Sorel (B. P. 242, 1900; *J. Soc. Chem. Ind.*, 1900, p. 337) distils the oil containing benzol by means of steam in a continuous-distillation column so constructed as to admit of separating the vapours into as many products as there are condensers employed, and thus varying the quantity and composition of each fraction at will. This he effects by partial cooling down to the temperatures of ebullition of the mixtures of steam and the single hydrocarbons concerned. At 93° C. nearly the whole of the xylene will escape condensation, but at 82° C. almost all the xylene will be condensed, without much toluene; at 72° a product very rich in toluene and heptylene will be condensed; below 65° almost all the benzene, without sensibly affecting hexylene or carbon disulphide.

Wilhelm (*Z. für chem. Apparatenkunde*, 1907, 1 and 33) discusses the various processes for absorbing the benzol from the coke-oven gas. The scrubbers, containing superposed sieves

for converting the absorbing oils into drops, are less expensive to work than the column apparatus, as these require a pretty strong pressure to force the gas through the liquid. The absorbing-oil, which takes up about 2 per cent. benzol, is first employed for cooling hot tar oils, and is thus heated up to 80° C.; after this it is treated with open steam in distilling-columns to expel the benzol. Before using it again for absorbing benzol, it is cooled down to 18° or 20° C. After having been in use for some time, its absorbing powers are reduced; it is then run into the tar-pit, and fresh tar-oil is introduced into the process. The crude benzol is rectified and purified in the usual manner (as described in this volume, Chapter XI.), and is sent out as pure benzene, toluene, xylene, and solvent naphtha.

At the Bulmke works of the Aktien-Gesellschaft für Kohlen-destillation A. Hüssener, the recovery of benzol from the gases has been greatly improved by cooling the absorbing-oils by means of a Linde cold-producing machine down to about 0° C. By this means up to 95·4 per cent. of the benzol contained in the gases has been recovered, the average being 93 per cent.

Kunow (Ger. P. 143307), very much like Hirzel, introduces the absorbing-oil into the gas by means of atomizing it, and employing a steam jet at the same time.

Recovering the Benzol from Coal-gas as Nitrobenzol.

Attempts have been made to extract the benzol from coal-gas in a different manner, namely, by *passing the gas through nitric acid*, or a mixture of nitric and sulphuric acids. This was patented by Leigh as early as 1863, but nothing came of it. The process was once more taken up by J. A. Kendal (U.S. P. 252473, of 1882), who first passed the gas through strong sulphuric acid, in order to extract from it those hydrocarbons [belonging to the "unsaturated" fatty series] which form an impediment to the ready nitrification of the benzene, which latter was effected by a second passage through a mixture of nitric and sulphuric acids. It is not possible to avoid the formation of dinitrobenzene; and Kendal, from the first, sets out with the intention of producing this compound as the

principal product. Evidently the process did not pay; and it was therefore modified in such a manner as rendered the previous removal of the unsaturated fatty hydrocarbons unnecessary (B. P. 1541, 1882). The coal-gas is passed through a superheater consisting of metal tubes partly filled with coke or charcoal and kept at a red heat. The flow of gas is regulated by a valve or meter to the point at which most benzol is produced for a given weight of gas. This is ascertained by passing a trial quantity through a vessel containing a mixture of 1 part of strong nitric acid and 5 parts of strong sulphuric acid up to the point where the change of colour shows the mixture to be saturated with benzol. The dinitrobenzene formed is precipitated by water, dried, and weighed. This test is repeated till the best proportions for the given case are found. As an instance, good results were obtained by passing 8000 cubic feet of gas per hour through nine cast-iron pipes, 8 inches wide, and each exposed to the heat for a length of 10 feet. The superheating process reduces the illuminating-value of the gas, but it is asserted to increase the quantity of benzol by from 5 to 40 per cent., and to make the gas fit for directly producing nitrobenzene or dinitrobenzene without a previous washing with strong sulphuric acid.

Kendal's process has been carried out on a manufacturing scale by Messrs Sadler & Co., of Middlesborough, who exhibited the products obtained by it at the Inventions Exhibition in London, 1885 (*J. Soc. Chem. Ind.*, 1885, p. 475). It evidently has the great drawback that most of the benzene is obtained as dinitrobenzene—a compound which is only employed to a limited extent in the manufacture of aniline colours. This process seems to have been abandoned again, after yielding somewhat considerable quantities of dinitrobenzene and dinitrotoluene.

Composition of Benzol obtained from Coal-gas.

Lunge and von Kéler (*Z. angew. Chem.*, 1894, p. 637) have analyzed two crude benzols from coke-ovens, one of which had been obtained by absorption, the other by the Heinzerling process, with the following results:—

I. *Benzol made by absorption.*—Clear, yellow liquid of un-

pleasant, tarry smell; spec. grav. at 16° = 0·875. Commences to distil at 18° C.; it yields the following fractions:—

	Per cent.		Per cent.
From 18° to 28° . .	0·01	From 81° to 91° . .	20·44
„ 28 „ 40 . .	0·26	„ 91 „ 100 . .	4·37
„ 40 „ 50 . .	0·15	„ 100 „ 111 . .	8·96
„ 50 „ 60 . .	0·50	„ 111 „ 140 . .	2·27
„ 60 „ 70 . .	1·62	„ 140 „ 150 . .	0·78
„ 70 „ 81 . .	58·92	Residue	0·62

Loss, 1·5 per cent.

II. *Benzol made by compression and cooling.*—Dark liquid, similar to "light-oil" from coal-tar; spec. grav. at 16 = 0·893. Begins to boil at 30°, and yields:—

	Per cent.		Per cent.
From 30° to 50° . .	0·01	From 120° to 140° .	4·20
„ 50 „ 60 . .	0·07	„ 140 „ 150 . .	6·25
„ 60 „ 80 . .	26·075	„ 150 „ 180 . .	2·67
„ 80 „ 90 . .	24·61	„ 180 „ 205 . .	3·91
„ 90 „ 100 . .	12·52	„ 205 „ 250 . .	4·35
„ 100 „ 110 . .	5·10	„ 250 „ 320 . .	0·45
„ 110 „ 120 . .	5·66	Residue (pitch) . .	1·50

Loss, 1·90 per cent.

The ultimate constituents of these distillates were separated as far as practicable by fractional distillations and by a number of chemical operations, described in the original; the final results are shown in the following table:—

Constituents.	Absorption-benzol.	Compression-benzol.
	Per cent.	Per cent.
Benzene	85·10	67·03
Toluene	11·63	15·61
Xylenes	1·54	2·18
Higher homologues	0·09	6·41
Naphthalene	...	3·79
Higher-boiling aromatic hydrocarbons .	...	1·42
Non-saturated fatty hydrocarbons . .	0·41	0·96
Thiophens	0·46	0·71
Phenols	0·08	0·11
Tar-bases	0·08	0·28
Carbon disulphide	0·01	...
Methyl-isocyanide	0·0024	...
Mercaptanes	0·00018	...
Residue	0·62	1·50

The difference between these two descriptions of benzol is undoubtedly caused by the fact that the absorption-benzol has left its high-boiling constituents in the absorbing-oil on redistillation.

Estimation of Benzene and its Congeners in Coal-gas.

Hempel and Dennis (*J. Gasbeleucht.*, 1891, p. 414) employed strong alcohol for absorbing the benzol contained in coal-gas. Dennis and O'Neill (*J. Amer. Chem. Soc.*, 1903, 503) found this unsatisfactory; they shake the gas during 3 minutes with an ammoniacal solution of nickel (16 g. nickel nitrate dissolved in 100 c.c. water + 2 c.c. concentrated nitric acid, and poured into 100 c.c. concentrated liquor ammoniæ). Before measuring the contraction, the ammonia vapours must be removed from the gas. To this Morton (*eod. loco*, 1906, xxviii., p. 1728) objects that that reagent had only the dissolving power of water or dilute ammonia for benzol; he, on his part, considers as the only proper method for estimating benzol in coal-gas, the absorption by sulphuric acid of specific gravity 1·84, a correction being made for the absorption of non-saturated aliphatic hydrocarbons. To this Dennis and M'Carthy reply in the same journal, 1908, xxx., p. 233. They now employ an ammoniacal solution of nickel cyanide which quantitatively absorbs the benzene from air or coal-gas. The reagent is prepared by adding a solution of 25 g. of potassium cyanide in 40 c.c. water to a solution of 50 g. of nickel sulphate crystals in 75 c.c. water, then adding 125 c.c. ammonia (specific gravity 0·91), shaking and cooling down to 0° C., in order to precipitate the potassium sulphate. Pour off the clear liquid and add a solution of 18 g. citric acid crystals in 10 c.c. water; allow to stand at 0° C. for 10 minutes, decant the liquid and transfer it to a Hempel pipette, the upper bulb of which is filled with broken glass. The gas to be analysed is passed in and out several times, and is then transferred to a similar pipette containing sulphuric acid, to remove ammonia. The nickel cyanide solution prepared as above does not absorb measurable amounts of ethylene or other constituents of ordinary coal-gas, except those which can be absorbed by potassium hydroxide solution. The authors find that the method suggested by Morton, as above quoted, does

not yield constant results. The strong sulphuric acid absorbs both ethylene and benzene, and presents difficulties in manipulation, by frothing to such an extent as to make the accurate reading of the gas volumes well-nigh impossible.

Harbeck and Lunge (*Z. anorg. Chem.*, 1898, xvi., 41) pass the gas through 110 c.c. of a mixture of equal parts of concentrated pure sulphuric and nitric acid, contained in a 15-bulb tube which retains the benzene as dinitrobenzene. The latter is separated by diluting and neutralizing the acid mixture; it is then dried and weighed. Pfeiffer (*J. Gasbeleucht.*, 1899, p. 697) employs this method in a somewhat simplified form. The same author later on (*Z. angew. Chem.*, 1905, 1156) shortens the process by titrating (instead of weighing) the dinitrobenzene; he reduces it by stannous chloride and titrates the excess of this with decinormal iodine and starch solution.

Haber and Oechelhäuser (*Ber.*, xxix., p. 2700), in a first operation, estimate the benzene and ethylene together in the usual absorptimetric way, and then ethylene itself, by means of bromine vapour, which combines with the ethylene, but not with the benzene vapour; so that the latter is found by difference. In 1900 Haber once more draws attention to this process and justifies its accuracy. He proceeds as follows. Determine the contents of a Bunte burette below the lowest division to the tap by weighing. Introduce about 90 c.c. of the gas to be tested and read off. Draw off all the water by aspiration exactly down to the tap, allowing a few minutes for the water adhering to the sides to collect, and drawing off this last drop as well. Pour about 35 c.c. bromine water from a stock bottle into a cup; allow 10 to 15 c.c. of this to enter into the burette; observe the volume in the burette, and allow a few drops of water to enter from below in order to force the bromine contained in the capillary below the tap into the burette. Incline and turn the burette so as to fill it with bromine vapour whose brown colour must prevail up to the end. After 2 or 3 minutes allow a strong solution of potassium iodide to enter, shake well, empty the contents of the burette into a beaker, rinse it with water, and titrate the free iodine by thiosulphate solution, noting the temperature and atmospheric pressure. Before and after this operation estimate the percentage of the bromine water in the stock bottle by titrating 10 c.c. with KJ and thiosulphate;

the average of those two tests, which ought to differ very little, is employed for calculating the result. One litre of decinormal thiosulphate = 1·121 litre of dry ethylene at 0° and 760 mm. The bromine water employed should be decinormal or even weaker.

Pfeiffer (*Chem. Zeit.*, 1904, 884) passes the gas through strong nitric acid, thus producing dinitrobenzene, which is either weighed or reduced by stannous chloride and titrated with iodine solution and starch.

Misteli (*Z. angew. Chem.*, 1905, 393) discusses various methods for the same purpose; so does Stavorinus (*J. Gasbeleucht.*, 1905, 272). He specially recommends the method of Dennis and O'Neill, who apply ammoniacal nickel nitrate (*Chemische Zeitschrift*, ii., 229).

B. *Tar (and Ammonia) obtained as By-products in Coke-making.*

We have seen above (p. 8) that more than a hundred years ago a somewhat successful attempt was made (by Stauf) to recover the tar formed in the coking of coal. It is not surprising that nothing further should have come of this; for in the first instance it must have been soon perceived that there was no profitable outlet for coal-tar at that time, and, moreover, it is very likely that the quality of the coke suffered under this kind of treatment.

For a long while after the extraction of tar and ammonia had been recognized as a very valuable accessory of gas-making, it was firmly believed that only inferior coke could be produced in this way, similar to what is obtained in retorts at the gas-works, and that the coke required for metallurgical purposes, more especially for blast-furnaces, could only be obtained in beehive-ovens or similar apparatus, untrammelled by contrivances for dealing with the gases or the condensable products contained therein. It had certainly been proved for some time past that at least the combustible gases escaping from the mouths of coke-ovens could be utilized in a more profitable manner than for illuminating the surrounding pit-heaps at night; and the improved coke-ovens constructed by Appolt, Smet, Coppée, and others had been for thirty years in general use in Germany, Belgium, and France, before in Great Britain anything seemed to shake the belief of iron-smelters in

the infallibility of the beehive-oven. But even on the Continent it was thought that, although the gases might be advantageously used for supplying the heat necessary for the destructive distillation of the coal, any attempt at condensing tar and ammonia must necessarily be fatal to the quality of the coke. This belief has long since been proved to be altogether unfounded.

The quantity of coal consumed in coking in Great Britain about 1890 was estimated at between eleven and twelve millions of tons per annum, against at most ten millions of tons distilled for gas-making. The quantity of volatile by-products hitherto left unused in coke-making amounted to about two millions of tons per annum. In the United States in 1896 nearly thirteen millions of tons of coke were manufactured, practically all in beehive-ovens, without recovery of tar and ammonia. Certainly, as we shall see below, the tar formed in the open beehive-ovens, which in Great Britain are the type almost universally adopted, is a substance very different indeed from gas-retort tar, and it is questionable whether its collection will always pay for the expense of it; but it is altogether different with the tar from the "close" coke-ovens long since introduced on the Continent, which tar is practically equal to normal gas-tar. This difference in the quality of the tar is caused by two circumstances, viz.:—first, that in the beehive-ovens and all similar ovens air is admitted into the coking-chamber, and, secondly, that the temperature in these ovens is very much below that obtained in the close coke-ovens and the gas-retorts.

The process of obtaining tar and ammonia as by-products in coke-making (not reckoning the abortive attempt of Stauf) originated in France, and remained stationary for a remarkably long time, until, all at once, about the year 1881, new interest was awakened in the subject, and it was taken up with almost feverish activity, more especially in Germany, but also in Great Britain, much less so in its original home, in France. It seems that the first apparatus of this kind was that constructed by Knab in 1856,[1] of St Denis, near Paris, at Commentry; but the

[1] Described in Armengaud's *Génie Industriel*, Aug. 1859, p. 71, and in *Dingl. polyt. J.*, vol. cliv., p. 97. Compare, with reference to the following historical notes, apart from the first edition of this work, also Gurlt, *Die Bereitung der Steinkohlenbriquettes*, p. 28; Hussener in *Stahl u. Eisen*, 1883, p. 397; and W. Smith, *J. Soc. Chem. Ind.*, 1884, p. 603.

condensation of tar and ammonia in these ovens was only later on introduced by Haupart and Carvès. The principal advantage of Knab's ovens was the increase of the yield of coke to 62·55 per cent., instead of the 54 or 56 per cent. previously obtained.

Knab's (or, rather, Haupart and Carvès') priority has been contested by a note in *Dingl. polyt. J.* (vol. ccl., p. 524), according to which there were fifty Pauwels-Dubochet coke-ovens at work near Saarbrücken as early as 1854; but Gurlt (in a letter to Mr Watson Smith, *J. Soc. Chem. Ind.*, 1884, p. 603) points out that no tar was then produced from the Dubochet ovens at Saarbrücken, all the gases and products of distillation being burned around the coking-chamber to heat it. From the description of the Pauwels-Dubochet ovens, which Oechelhäuser examined in 1860 during a visit to the La-Villette works of the Paris Gas Company,[1] it would appear that they had then been for some time in use for the production of excellent metallurgical coke, along with rather poor illuminating-gas, which was mixed with the richer gas made in ordinary gas-retorts. The temperature in those ovens was much lower than in the Knab ovens. Tar and ammonia must necessarily have been condensed, since the gas was required for illuminating purposes; in fact, E. A. Behrens, who subsequently describes the same plant,[2] mentions that the yield of tar was 4·67 per cent., and that it was much lighter than retort-tar, and poorer in naphthalene and phenols. [The specific gravity (1·2) given for that tar is probably erroneous.] The Pauwels-Dubochet ovens seem to have been introduced merely on account of the higher value of the coke (at that time 35 fr. per ton, against 20 fr. for retort-coke), and appear to have been abandoned at La-Villette for some time past.

About the same time (1861) patents were taken out by Jones and by Blackwell for obtaining, by simple contrivances, tar and weak ammoniacal liquor when coking coal in pile. As might have been anticipated, these attempts were not crowned with any success. Jones's plan has been described by Watson Smith.[3]

Knab's original furnaces only possessed bottom flues beneath

[1] *Dingl. polyt. J.*, vol. clx., p. 394; *Wagner's Jahresber.*, 1861, p. 674.
[2] *J. prakt. Chem.*, vol. ccvi., p. 277.
[3] *J. Soc. Chem. Ind.*, 1884, p. 604.

their beds. A considerable improvement was effected by Carvès, under whose management 88 Knab ovens were erected at St Etienne, which, however, were abolished later on. Carvès, at Commentry, first introduced the heating of the ovens by side flues in addition to the bottom flues. A description of those furnaces, as they were working in 1862, has been given by Gaultier de Claubry[1]. The gases and vapours escaping from the closed coke-ovens were passed into a hydraulic main cooled by air, where tar and ammonia condensed, while the gases were continually drawn off by exhausters, and employed for heating the coke-ovens, by issuing from an annular burner along with air admitted into its inner space. In order to collect the condensable products more completely, the gas was first passed through coke-scrubbers fed with water, and then through a set of 500 upright lead pipes of $\frac{3}{8}$-inch width, externally cooled by water.

The Knab-Carvès ovens were gradually introduced into other places. In the years 1866 to 1873, 53 such ovens were erected at Bessèges, and 100 ovens at Terre-Noire, near St Etienne, 1879.

The Bessèges coke-ovens have been minutely described by Dr Angus Smith,[2] who, with very great foresight, warmly recommended this system at a time when hardly anybody in Great Britain had taken any notice of it.

Further attention was drawn to the Carvès ovens by Mr H. Simon in a paper read to the Iron and Steel Institute in May 1880, but without making an immediate impression.

The Carvès ovens, as they were working at Bessèges in 1880, have been accurately described and figured in the *Bulletin de la Société de l'Industrie Minérale*, vol. ix., p. 283.[3] After many trials they were made only 2 feet wide, to allow of the heat penetrating them thoroughly. Over a small fire-grate is placed the mouth of a pipe conducting the gases formed in coking, from which tar and ammonia have been abstracted, and here they are burned. The products formed in combustion pass underneath the hearth of the oven, then travel upwards to the top-

[1] *Bulletin de la Société d'encouragement*, 1862, p. 581.

[2] *Fourteenth and Fifteenth Reports on the Alkali Acts*, for 1877 and 1878, pp. 49 *et seq.*

[3] Quoted through *Dingl. polyt. J.*, vol. ccl., p. 254.

most of the three flues built in the side-walls, and downwards through these flues into the main flue leading to the chimney. The volatile products escape through a pipe from the interior of the coking-chamber; they first pass through a number of horizontal pipes, cooled by a stream of water, and then through scrubbers, where they are freed from tar and ammonia previously to being introduced into the combustion-chamber.

The most recent modifications of the Carvès ovens will be described subsequently.

Pernolet's coke-ovens[1] are very similar to Knab's. From Gurlt's description (*loc. cit.*) it would appear that they were kept at a greater heat than Knab's. The condensing-plant for tar and ammonia was added to them by Benut and Renant, and seems to have been very well constructed, but a very unfavourable account of the working of the ovens themselves is given by Stevenson.[2]

In 1873, H. Aitken, of Falkirk, conceived the idea of drawing off tar- and ammonia-vapours from beehive-ovens, which was further developed in 1879.[3]

In 1879, Ströhmer and Schultz (Ger. P. 8174) proposed drawing off the gases and vapours from coke-ovens by a sliding tube before they had time to be decomposed by the heat of the brickwork. Lest the quality of the coke should suffer by the gases being drawn off too fast, the sliding tube was raised or lowered by an automatic pressure-regulator. This plan was tried at Plauen, near Dresden, but without success.

In 1880, H. C. Bull patented an oven somewhat similar to Aitken's.

About that time Ed. Fischer constructed an oven for obtaining tar and ammonia from bituminous shale, and more particularly from the browncoal breeze found in enormous quanties in Bohemia in the shape of pit-heaps. The process is said to have answered well, but only yields an inferior coke, fit for heating domestic stoves.[4]

Up to the year 1881 none of the processes for obtaining tar and ammonia in coke-making had been found to be thoroughly

[1] Armengaud's *Génie Industriel*, June 1870, p. 281; *Dingl. polyt. J.*, vol. cxcvii., p. 411.

[2] *J. Soc. Chem. Ind.*, 1883, p. 604.

[3] Watson Smith, *ibid.*, 1884, p. 604.

[4] Hüssener, *Stahl. u. Eisen*, 1883, p. 409.

successful, especially with respect to the quality of the coke, so that a prize offered in 1870 by the Berlin Society for the Advancement of Industry was allowed to lapse. The only exception to this rule, the Carvès oven, had not become sufficiently known outside a comparatively small circle. Whilst many different ovens were known which utilized the heat of the gases evolved, and indeed such ovens were very generally employed on the Continent, the further problem of recovering the tar and ammonia without in any way injuring the quality of the coke for blast-furnace purposes was tacitly or expressly regarded as insoluble.

In 1881, the coke-making public in England and Germany almost suddenly became aware that the long-standing success of the Carvès oven was a reality, and that these ovens could even be improved upon. In England Mr H. Simon, of Manchester, assiduously laboured for the introduction of Carvès' process, improved by a recuperator. We shall not here attempt to give a description of all the new coke-ovens patented during the last few years, more particularly since it would involve a corresponding number of diagrams; we shall merely give an enumeration of the different patents, along with a reference to the places where the descriptions are to be found, and we shall then select a few of the most important and most widely adopted plans for special description and illustration. We shall not give any account of such inventions as are only intended to utilize the coke-oven gases for heating-purposes, in order to increase the yield of coke.

Patents for coke-ovens with recovery of tar and ammonia have been obtained by:—

Ströhmer and Schultz (Ger. P. 13395 and 16807).

H. Aitken (B. P. 2682, 1882).

U. Hegener (Ger. P. 13996).

Th. Hornig (Ger. P. 21908 and 23670).

F. Lürmann (Ger. P. 13021, 15512, 16134, 16741, 17055, 17179, 17203, 17661, 18128, 18927, 20205, 20211, 22602, 29088, 29557, 31660).

L. Semet and E. Solvay (Ger. P. 18935). Experiments made with their ovens by Ch. Demant are described in the *Revue Universelle des Mines*, vol. xiii., p. 593; Wagner's *Jahresbericht*, 1883, p. 1220.

G. Hoffman (Ger. P. 18795).

C. Otto & Co. (Ger. P. 13156, 16436, 16840, 19040, 20908, 24586, 31004, 31590, 34431, 37062, 37280). Their ovens will be described in detail below, as those most generally employed in Germany.

J. Jameson (B. P. 1947, 5076, and 5498, all of 1882; Ger. P. 24915, 25676, 27694). His coke-ovens are the most energetic attempts at combining the beehive-oven with a recovery of the by-products, and will be described below.

A. Hüssener (Ger. P. 16923, 20196).

H. Simon (as communicated by F. Carvès: B. P. 554, 1883; 15920, 1884).

H. Simon and Watson Smith (B. P. 4871, 1883).

H. Hutchinson (B. P. 2843, 1883).

O. Ruppert (Ger. P. 24404, 26307).

R. de Soldenhoff (Ger. P. 25824; B. P. 11967, 1885).

A. Klönne (Ger. P. 25673).

Hiltawski and Kahnert (Ger. P. 24438).

Schlesische Kohlen- und Kokswerke in Gottesberg (Ger. P. 25825, 26421).

H. Herbertz (Ger. P. 15086, 17873, 25526, 27506, 31906, 34286).

Th. Bauer (Ger. P. 28530, 32235, 32660).

Th. Nicholson (B. P. 358, 1884).

C. E. Bell (B. P. 443, 1884).

J. McCulloch and Th. Reid (Ger P. 31158).

A. M. Chambers and T. Smith (B. P. 4708, 1884; and B. P. 7358, 1885).

H. Stier (Ger. P. 26897, 35120).

F. Wittenberg (Ger. P. 26132).

A. Zwillinger (Ger. P. 29888).

Gebrüder Röchling (Ger. P. 33956, 35001).

Lothringer Eisenwerke at Ars (Ger. P. 32841).

J. Quaglio (Ger. P. 36357).

J. Schmalz (Ger. P. 37182).

Descriptions of most of these patents have been collected by F. Fischer in *Dingl. polyt. J.*, vol. ccxlviii., p. 249; vol ccl., pp. 456 and 521; vol. cclii., pp. 253 and 283; vol. ccliii., p. 372; vol. cclvi., p. 359.

These are translated in the *J. Soc. Chem. Ind.*, 1884, pp. 101, 505, 510, 531; 1885, p. 484.

A synoptic table of the ovens known up to 1884 has been given by Watson Smith, *eod. loco*, 1884, p. 605 (also in the *Journal of the Iron and Steel Institute* of that year, with a table of diagrams and many further particulars).

The following is a list of the German patents taken out since:—

Gebrüder Röchling, No. 38312.
J. Collin, No. 36518.
Dr. C. Otto & Co., No. 37280.
F. Ströhmer, No. 46595.
Dr. C. Otto & Co., No. 50982.
F. Brunck, No. 51518.
C. Otto and F. W. Lürmann, No. 52206.
W. Fritsch, No. 52134.
O. Dilla, No. 53860.
M. Kleist, Nos. 56488, 56489, 59635.
The Economic Gas and Coke Co., No. 59893.
F. Stauber, Nos. 61532, 67189.
J. Leschhorn, No. 67099.
G. Martin, No. 72103.
F. Brunck, No. 73504.
Th. Bauer, No. 73701.
G. Magirino, No. 78927.
C. Otto & Co., Nos. 80145, 82000.
T. J. Collin, No. 80820.
H. Stinnes, No. 88389.
C. Otto & Co, No. 90499.
Aktienges. f. Kohlendestillation, No. 94040.
Wechselmann, No. 103508.
Festner & Hofmann, No. 103577.
Dillon de Micheroux, No. 104229.
Brunck, No. 107864.
Dr. C. Otto & Co., No. 105432.
Ditto No. 106959.

Some more recent patents will be mentioned below.

Abstracts from these specifications and their English equivalents are given in the successive volumes of the *J. Soc. Chem. Ind.*

Very important papers on many of these coke-ovens, with exact diagrams, have been published by A. Hüssener (*Stahl u. Eisen*, 1883, p. 397), C. Otto (*eod. loco*, 1884, p. 396), P. Lürmann (*ibid.*, 1892, p. 186), G. Hilgenstock (Glückauf, 1896, p. 497), R. Remy (*Z. angew. Chem.*, 1890, p. 327), A. Dannenberg (*ibid.*, 1894, p. 352), Truchot (*ibid.*, 1898, p. 263), Hilgenstock (*J. Gasbeleucht.*, 1902, 617), Beilby (*J. Soc. Chem. Ind.*, 1899, 643). A finely illustrated volume has been issued by the United States Coke and Gas Company, on *The Destructive Distillation of Bituminous Coal*, 1906.

We may with Watson Smith (to whose valuable contributions I am indebted for some of the following information) fitly class the various forms of recovery coke-ovens (as we shall style those ovens which aim at the recovery of tar and ammonia) as being derived, consciously or not, from three "root-forms," namely—first, the beehive, a sort of covered-in meiler or mound, into which air is admitted so that some of the coke is burned as fuel for the remainder; secondly, the Coppée oven; and thirdly, the Knab-Carvès and Pauwels-Dubochet coke-ovens. The two latter belong to that class of coke-ovens which we may call horizontal closed ovens; both of them are so constructed that the gases evolved during dry distillation are utilized for heating the ovens from without, no air being admitted into the coking-chamber itself. The principal difference between the Coppée and Knab-Carvès ovens is as follows:—the former are provided with a large number of openings in the upper part of their side-walls, connected with an equal number of parallel heating-flues running perpendicularly downwards between each two ovens, and into these flues air is admitted, the flame ultimately passing below the sole. The Knab-Carvès ovens, as well as the Semet-Solvay ovens, are heated by flues running horizontally in a zigzag form, also between each two ovens.

The upright ovens of the Appolt system have also been adapted to the recovery of tar, etc.; but we shall not deal with these, as they do not seem to have been very widely used.

I. *Modified Beehive-Ovens.*

To the beehive form belong the Meiler arrangements of Jones and of Blackwell, where tar and ammonia were collected

by underground pipes, but the gases were passed upwards by the central stack and were lost. Real beehive-ovens, modified for the recovery of tar and ammonia, are those of Aitken and Jameson, which bear much resemblance to each other. Aitken blows air into his oven above the coke, along with the return gas from the condensing and scrubbing apparatus, and he exhausts the gases and vapours, drawing them downwards through the bottom of the oven by means of three perforated flues through which the gases and products pass, uniting in one main, before proceeding to the condensing-apparatus.

The special object of Jameson's invention (B. P. 1947 and 5076, 1882) was to utilize the existing beehive-ovens as much as possible, merely adapting them to the recovery of tar and ammonia. He places an exhaust pipe with tap below the soles of his oven, and in addition to this he provides two other smaller pipes, through which the gases and vapours are returned at suitable intervals. The oven is filled as usual, and as soon as ignition has taken place above, the wider suction-pipe is caused to act gently, effecting a slow exhaustion of the by-products and gases. Since this process diminishes the quantity of the coke and makes it softer, Jameson conveys through the other pipes a portion or the whole of the gas drawn off, and a portion or the whole of the tar-vapours, to a similar oven, but one which has attained a further stage of combustion and ignition, in order that the carbon of the gases and vapours may become deposited in the pores of the coke thus treated, whilst the hydrogen burns at the surface of the mass or escapes. He claims various other possible modes of action and treatment of gas and by-products (such as the addition of pitch deprived of its valuable portions).

Jameson further proposes (B. P. 5498, 1882) to treat carbonaceous or coaly matters, shales, etc., difficult or impossible to coke, such as "duff-coal" or pit-heaps, also on the partial-combustion principle in an oven which partakes of the nature of a reverberatory furnace. It resembles a modified beehive-oven, with a fireplace and reverberatory-furnace fire-bridge attached, so that the flames from the furnace can play over the thick coking-mass on the deep-lying oven-bed, and then pass on to the chimney-flue, whilst the suction process for gases and by-products is set up in the space below the perforated bed on

which the coking-mass lies. He also proposes to adapt this process to the roasting of ores in order to recover by-products, and for the recovery of fairly pure carbonic acid from limestone or in sublimation.

Particulars concerning the working of the Jameson ovens are given by the inventor himself in the *J. Soc. Chem. Ind.*, 1883, pp. 114, 228, and 405; and 1885, p. 314. He states a good many objections to the use of gas for heating coke-ovens from without, to which he prefers burning the surface coke by means of the downward suction employed. We will not enter into his theories, so many facts pointing the other way; his own ideas as to the use of the gas evolved in coking for other purposes were confessedly very imperfect. The average yield per ton of coal is estimated by W. W. Pattinson at 10 lb. of sulphate of ammonia, 8 gall. of oil, and 12,000 cub. ft. of gas. The cost of plant per oven, that is the addition of the new parts, varies from £10 to £20. The yield of coke is, "if anything, rather greater than in the ordinary oven," say 10 to 13 cwt. from one ton of Northumberland small coal, or 67½ to 70 per cent. from Durham coking-coal [in any case very much below that obtained with closed ovens of the Coppée or Carvès type].

In the paper read in 1885 (*J. Soc. Chem. Ind.*, 1885, p. 314), Jameson discusses the reasons why his process, although it fell into the hands of the ablest of practical men, and was worked out in a great number of places, with no regard to expense, had not realized the anticipations of its inventors and its promoters. Modifications are described for making the oven bottoms more nearly air-tight, and for cooling the gas in order to increase the yield of ammonia and oil.

We shall see further on that the *tar*, or rather (as Jameson himself calls it) the "oil," produced in the Jameson ovens is altogether different from gas tar, being a low-temperature product, and is principally composed of paraffinoid hydrocarbons, such as exist in shale-oil, browncoal-tar, etc. But it is much less valuable than the latter; since its specific gravity is very high, there is very little chance of utilizing it for the manufacture of burning- and lubricating-oils, and the idea of "improving" it by passing it through red-hot tubes, as patented by C. E. Bell (B. P. 9510, 1884; extended to blast-furnace tar by B. P. 12681,

1884), and advocated by Armstrong (*J. Soc. Chem. Ind.*, 1885, p. 451), is thoroughly impracticable, as will be shown later on. Hence the Jameson tar must be regarded as of very little value.

There is also no doubt that the yield of *ammonia* from the Jameson ovens is not very high, decidedly less than from closed coke-ovens. Obviously the admission of air is very prejudicial in that respect, although the low temperature of the Jameson oven ought to favour the formation of ammonia in other respects. It is also evident that some of the ammonia is directly burned.

We will mention only one more attempt in a similar direction. H. Hutchinson (B. P. 2843, 1883) believes it possible to obtain at will hard coke along with tar rich in benzol by causing a rapid rise in the temperature of ignition, or a soft coke along with tar rich in paraffin by slow coking. The former he proposes to effect by passing previously heated air through numerous channels or small flues into the ordinary coke-ovens, in order to hasten the coking and raise the temperature of ignition, the by-products being drawn off by flues in the upper part of the ovens. [That tar produced under such circumstances should be "rich in benzol" is very doubtful.] He also proposes producing heating-gas or illuminating-gas by passing, along with the air, superheated steam through a perforated tube rising in the centre of the oven amongst the fuel.

In any case we may here state it as an admitted fact: *that no coke-oven of the "open" kind, where air is admitted into the coking-chamber, yields tarry products similar to ordinary coal-tar —that is, such containing a considerable quantity of benzene, naphthalene, anthracene, and other aromatic hydrocarbons, employed as first materials in the manufacture of artificial dyes and colours.*

Some of the recovery-ovens retain the form of the *beehive, but so modified that the oven becomes a closed one*, no air being admitted into it, whilst tar and ammonia are evolved, all the heating being then done by the return-gas. This is the case with one of the ovens constructed by Pernolet, and also with that of Klönne (Ger. P. 25673). The latter draws off the gaseous products from the top and heats the bottom of the oven by the return-gases remaining after condensation, till all the tar and ammonia are drawn off as far as possible. Then the second stage of the process is started by conducting the gases, instead

of through the hydraulic main, into a vertical side-flue, some air being admitted at the same time in front of the lower part of the oven, and the partially burnt gases being completely burnt later on by air previously heated. This oven thus forms a connecting link between open and closed coke-ovens; it does not seem to have been employed to any great extent.

The problem of adapting beehive coke-ovens to the recovery of by-products seems to have approached a better solution, by entirely doing away with the old method of coking by partial combustion of the coal, and applying all the heat from without by means of bottom-flues, the necessary degree of heat being attained by a previous heating of the combustion-air in Siemens's or other "recuperators." This is done in the ovens patented by C. Otto & Co., and the Hibernia and Shamrock Coal Company, and erected at the Shamrock pit in Westphalia in 1886 (Ger. P. 37280). There are two recuperators placed side by side in the wall, between two sets of coke-ovens. One of these stores up the heat of the fire-gases passing through it, while the other transmits the heat, already received, to the air which is to maintain the combustion of the residual gases in the bottom-flues. Once an hour the direction of the draughts is changed, so that the two recuperators mutually exchange their mode of working. The gases given off in the coking-chambers are drawn off by a pump, and forced back into the flues below the soles of the ovens. Between the escape-pipe, which is situated in the crown of the oven, and the pump, there is a hydraulic main, and the usual condensing and scrubbing arrangements, just as constructed for the Coppée-Otto ovens (pp. 71 *et seq.*). At the Shamrock pit each oven carries a charge of 4 tons, and gets through it within 55 hours; the yield is 80 per cent. of large-sized coke (against 65 to 68 per cent. obtained by the old process), 5 or 6 per cent. of tar, and 1 per cent. of sulphate of ammonia; also 244 cubic metres (say 8540 cubic feet) of gas per ton of coal. The quality of the coke is altogether as good as that of the ordinary beehive coke; the reason why this is the case, in spite of the heat being exclusively communicated by means of bottom-flues, is probably connected with the fact that the coal is spread in a comparatively shallow layer over the oven-sole, and the very large increase of yield is hence an entire gain. Besides this, the

time occupied in coking the charges is very much reduced, and the by-products obtained are a further gain.

According to information derived from competent sources, it appears that the object of the above-described invention is solely the better utilization of existing beehive-ovens, by adapting them to the new system (which is a rather expensive process); but nobody would think of building ovens of this kind without regard to the tar product, for the simple reason that the discharging of beehive-ovens is decidedly more troublesome than that of horizontal coke-ovens. Nobody in Westphalia seems to doubt that the latter are the best coke-ovens, and that beehive-ovens will be discontinued altogether in the course of time.

II. *Recovery-Ovens on the modified Coppée System.*

A very remarkable oven of this class is that of Lürmann, differing from all others in the continuous style of work adopted in it.[1] The oven, which, like all other Coppée ovens, forms a narrow channel of moderate height and of considerable length (say 30 ft.), consists for two-thirds of its length of a heating- and coking-chamber, and for the last third of a storage-chamber. The front of the first chamber is closed by a door in the shape of a ram, moved alternately backwards and forwards. The coal to be charged falls down from a hopper in front of the ram, and is by this pushed into the oven, forcing on the charge already contained in the oven towards its other end, where the finished coke collects and is taken out by a discharging apparatus. The gases and vapours pass away from the centre of the coking-chamber through a hydraulic main, and, after condensing the tar and ammonia, are used for heating the coking-chamber from without, the thickness of the walls being reduced to 2½ or 3 inches, the numerous partition-walls of the flues bracing them up to a sufficient extent. The whole is always under a considerable pressure, produced by the ram. The cooling of the walls during the charging and discharging, unavoidable in all other ovens, is here done away with: since the same quantity of coal is always in the same

[1] I take the description and criticism of this oven from Hussener, *Stahl u. Eisen*, 1883, p. 401, where a good diagram is also given.

stage of distillation, the quantity and quality of the gas is invariably the same throughout the process; the details of the construction are such that a very high temperature can be maintained at will all over the coking-chamber. Owing to this and the high pressure, it has been found possible in the Lürmann oven to make hard smelting-coke from very dry, anthracite-like coal, the smalls of which are otherwise of hardly any use; but it is best to mix this with half its weight of ordinary coking-coal. It is not adapted to coking-coal without the admixture of dry coal. It would seem from this description as if the Lürmann ovens were the most perfect of their kind, at least so far as the coking proper is concerned, and a goodly number of them have actually been erected in Westphalia; but they have not answered their purpose, and have been stopped, as the quality of the coke was not satisfactory and the discharging-apparatus showed serious drawbacks. Lürmann, in the discussion following the reading of the paper (*Stahl u. Eisen*, 1883, p. 412), points out that his oven is not intended to compete with those destined for the ordinary descriptions of coking-coal; that it produces excellent coke from coal which is otherwise quite unfit for that purpose; that this coke is especially good for cupola-furnaces (as proved by certificates); and that his ovens yield tar and ammonia from coals otherwise useless for coking-purposes. It would appear that the quantity and the quality of the tar and ammonia recovered in Lürmann's ovens have not been at all accurately ascertained, and we must therefore dismiss them for the present from our consideration.

Otto's first modifications of Coppée's oven for recovery purposes have been superseded by his later adoption of Hoffmann's principle, noticed below. We also refer the reader to the patent specifications and to the extracts in *Dingl. polyt. J.*, and those given by Watson Smith, for the ovens patented by Herbertz, R. de Soldenhoff, and others, belonging to this class, none of which have met with an extensive application.

The most successful kind of oven, as regards the number introduced and the results obtained in Germany, is that originally patented by Gust. Hoffmann (Ger. P. 18795), based upon a proposal of Th. von Bauer, and modified by Dr C. Otto & Co. by a number of additional patents (*cf.* p. 64). The essential feature of this plan is a combination of Siemens's

recuperators with the ordinary Coppée oven, provided with a number of improvements in details. The following is a description of these ovens, principally from the paper published by Otto in *Stahl u. Eisen*, 1884, p. 396, but with modifications to suit later patents; the diagrams are taken from the working drawings kindly lent to me by Dr Otto.

Fig. 6 is a longitudinal section through the centre of an oven; Fig. 7 a longitudinal section through the flues between each two ovens; Fig 8 a tranverse section through a number of ovens. The letters show the same parts on all the diagrams.

These ovens are from 30 to 33 ft. long, 2 ft. wide, 5 ft. 3 in. high to the abutment of the arch, with a 4-in. taper, and 2 ft. $11\frac{5}{8}$ in. from centre to centre. In lieu of the side openings through which, in ordinary Coppée ovens, the gases pass out of the coking-chamber down the sides and underneath the bottom, in order to be burnt, there is here no direct connection between the coking-chamber and the side of the oven; apart from the end doors for charging and discharging (*a* and *b*), closed during the operation, there are only two openings in the top arch, *c c*, through which the distillation gases and vapours can escape. In the side-walls below the abutment there is a horizontal flue (*d*) passing along all the vertical side-flues and connecting them. Each bottom-flue in the length of the oven is divided midway by a partition (*e*) into two equal halves (*f* and *g*). Each of these half-flues communicates with a recuperator (*h* or h_1), destined for heating the air necessary for the combustion of the heating-gas. The recuperators are long chambers, filled with an open network of bricks, and reaching along the whole range of ovens. At the end of the range the two recuperators, *h* and h_1, by means of a throttle-valve, are made to communicate either with the fan-blast conducting air or with the chimney.

When the ovens are charged and the coking is in progress, the gases evolved from the coal escape through the openings *c c* in the oven-arches into the tubes *i i*, and then pass into the main receivers *l l*, the valves *k k* being left open. From the receivers *l l* the gases pass to the condensing-plant, where they are freed from tar and ammonia in the gas-coolers and in the scrubbers, as will be described below. The same exhauster which drew the gases to the condensing-apparatus now forces them back towards the ovens into the tube *m*; and from this, according to

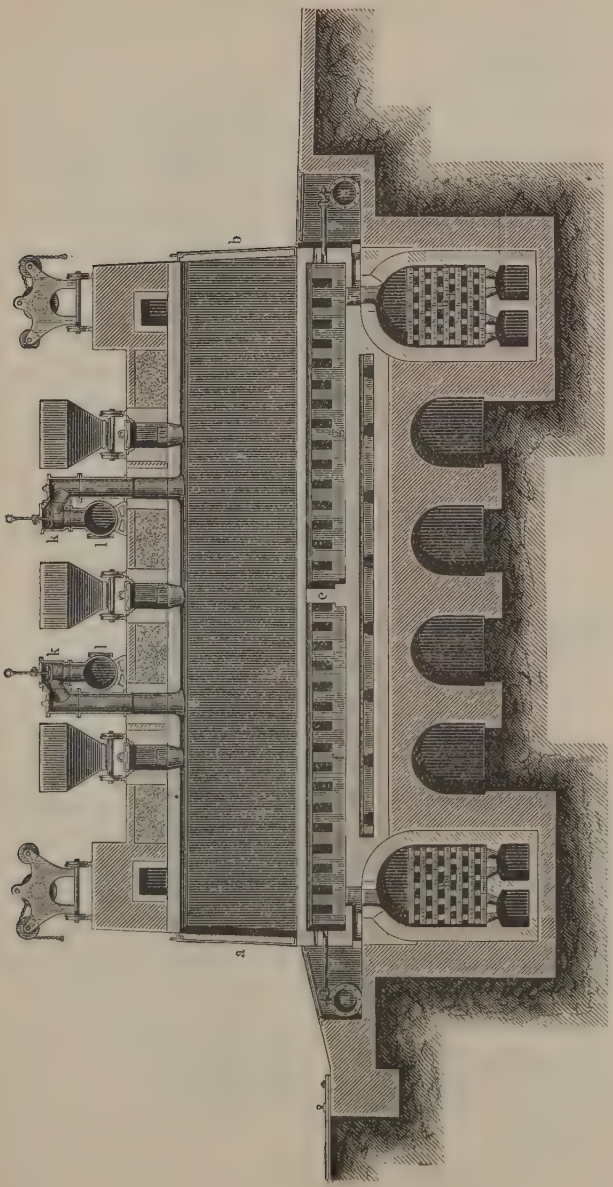


FIG. 6.

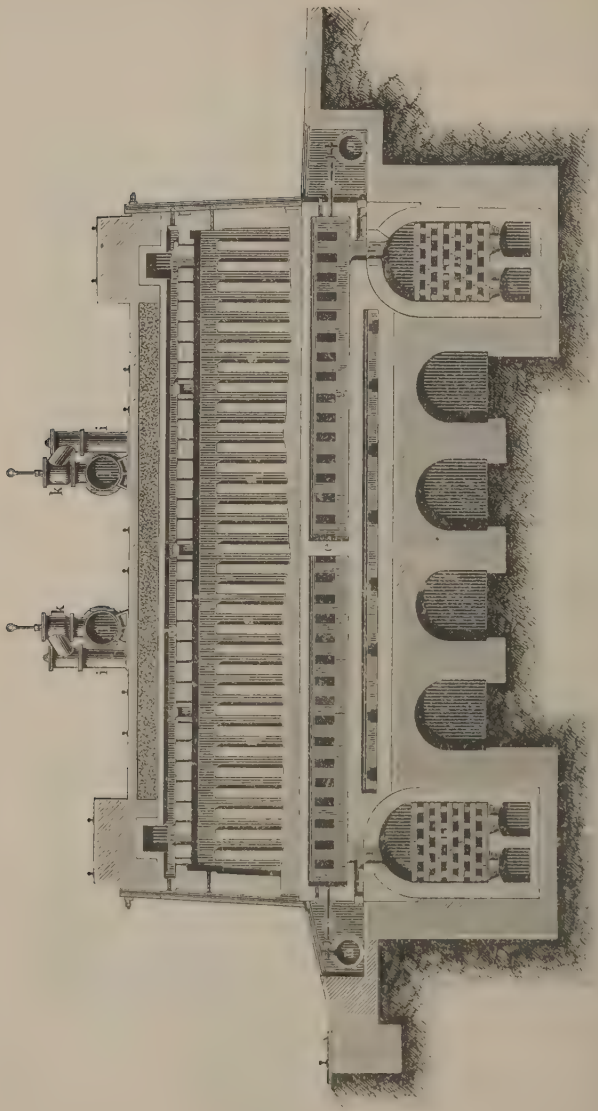


FIG. 7.

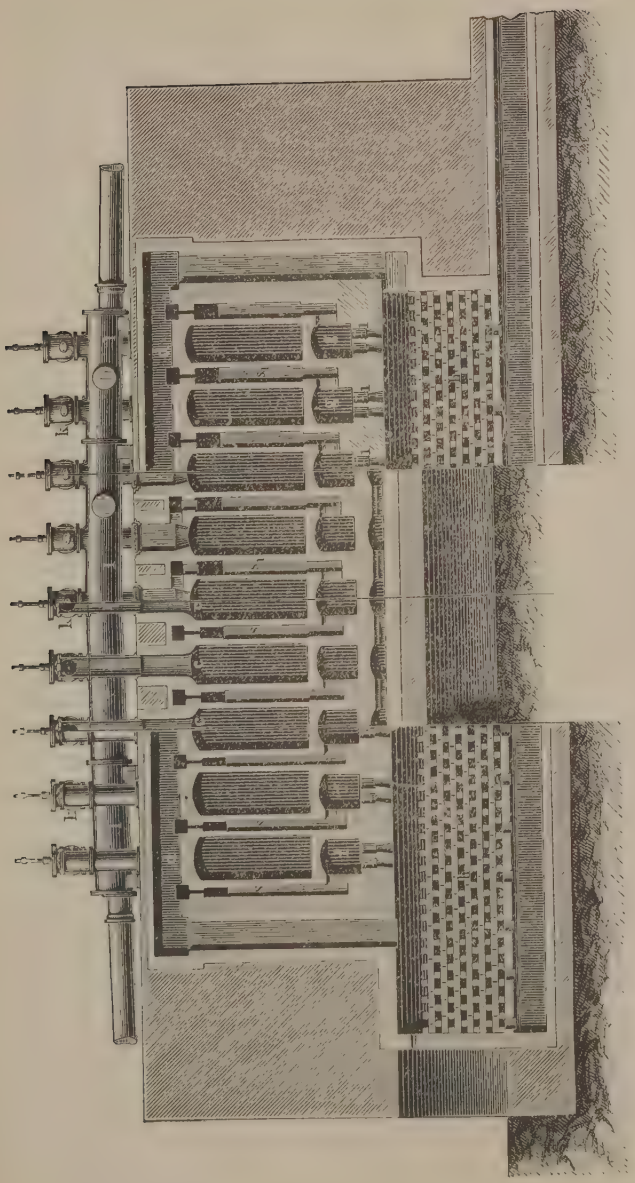


FIG. 8.

the position of the throttle-valve, either into the tube *n*, on the one side of the oven-range, or into the tube *o*, on the other side of the range. At each oven the tubes *n* and *o* communicate with the bottom-flue *f* and *g* by means of a small inlet-pipe (*p*) provided with a tap.

Suppose the gas is passed into the pipe *n*, on one side of the oven-range, the throttle-valve of the recuperators is placed so that the air (which is forced in by means of a fan-blast) enters at the same side into the recuperator *h*, which communicates opposite each oven, by openings *r r*, with the bottom-flue *f*. Thus both gas and heated air enter into the bottom-flue *f*, the combustion taking place partly in this flue, partly further on. The current of burning gases and very highly-heated combustion products passes upwards by the parallel vertical flues *s* into the upper horizontal flue *c*, and on the other side of the ovens by the parallel vertical flues s_1 downwards into the bottom-flue *g*, from which the gases, now completely burned, pass through the recuperator h_1 into the chimney, and on their way give up their heat to the network of bricks. After a certain time, say an hour, the throttle-valves are reversed, and the gaseous current now travels in the opposite direction: the return-gas from the condensing-plant enters into the tube *o*, the air into the recuperator h_1, the combustion takes place in the bottom-flue *g*, the products pass through the vertical flues s_1 upwards into *c*, and thence through the vertical flues *s* downwards into *f*, and at last through the recuperator *h* into the chimney.

Dr Otto points out that, owing to the slow conductivity for heat of fire-bricks, the air in Siemens's recuperators, worked alternately in opposite directions, is heated incomparably more quickly and highly than in those recuperators where the hot combustion-products travel on one side, the air is heated on the other side of a brick partition, and the current of gases always flows in the same direction.[1] In the Otto recuperators the temperature of the air rises to 1000 C.; and the effect of this is that the cold gases, deprived of their tar, as they return from the condensing-plant, are far more than sufficient for carrying out the coking-process. If they were all to be burned, the ovens would get much too hot; and it is found that there is an excess of 200 cubic metres (say 7000 cubic feet) of gas per oven per

[1] This is contradicted by Simon, *cf.* below.

day which can be utililized in other ways. With a normal charge of 115 cwt. of dry coals per oven the coking-process is finished in 48 hours, but sometimes less, so that the quantity of gas must be diminished to bring the time up to 48 hours. Since both gas and air are blown in mechanically, it is quite easy to regulate the process at will.

The quality of the coke made in these ovens is altogether excellent; the yield considerably exceeds that formerly got from the same coal in Coppée ovens, without recovery of tar and ammonia. Calculated upon coal containing 10 per cent. water, it was formerly 61 per cent., and is now 68 per cent.; that is, upon dry coal, 67·7 and 75·56 per cent. respectively. Dr Otto attributes this result to the absolute air-tightness of the ovens, along with a slight over-pressure. The temperature, as measured by a Steinle and Hartung's graphite pyrometer and controlled by the fusing of metallic alloys, was found to be 1200° to 1400° C. in the bottom flue, 1100° to 1200° C. in the side flues; 1000° in the recuperator at the time the air-current is admitted, and 720° when it is shut off; 420° in the chimney.

Of the Otto-Hoffman ovens, as described just now, up to 1894 already over 1200 were constructed on the European Continent, more than three times as many as existed there of any other type of by-product oven. In 1894 they were introduced into America by the Otto-Coke and Chemical Company, and later on by The United Coke and Gas Company. Up to 1905, 2780 of these ovens had been built by them in various States of the Union, the surplus gas being used for fuels, power, and illumination. The United Coke and Gas Company, New York, claim that the surplus gas from their ovens gives a higher candle-power from the uses of coal than can be obtained when the coal is distilled in the ordinary gas retorts. They apply to the gas a system of coolers and washers similar to that which is usually employed for blast-furnace gases (see later on). Schniewindt (*J. Gasbeleucht.*, vol. xliii., p. 53) makes more detailed communications on this system which is said to work most successfully, the "rich" and the "poor" gas being purified in quite separated sets of apparatus.

The "Rothberg" oven is of a similar type. In 1904, 94 of these were in operation at Buffalo, and 141 in course of construction.

Otto-Hilgenstock Ovens.

In the course of time the Otto ovens have been improved in many respects, as to the more regular distribution of the heat, speedier finishing of the charge, and greater freedom of the masonry from repairs. We cannot go into details about these improvements, concerning which reference must be made to the above-enumerated patents.

We must, however, give the description of a coke-oven, later on patented by Messrs C. Otto & Co. (Ger. P. No. 88200), in which the recuperator is abandoned and heating by gas from the bottom is introduced. According to authoritative information, these ovens, known as the Otto-Hilgenstock ovens, of which up to the end of 1897 already 400 had been erected, do considerably better work than the former constructions, owing to the production of heat taking place all along the length of the oven. The air for combustion is in a very simple manner heated in the foundation of the oven, so that no heat is lost there. There is no necessity for blowing in the air by machinery, and the gas is under such low pressure that all conditions are present for a good recovery of the by-products. The gas is conveyed in piping, laid underneath the ovens in an accessible way, and is from there introduced into the heating-flue by tuyeres. As shown in Figs. 9 to 11, the walls forming the foundation are conveniently arranged so as to run parallel to the length of the ovens, and are covered with an arch for each two ovens. The passages and flues, arranged in the foundations, are large enough to be accessible to workmen. In these passages are placed the gas-pipes, *g*, with their tuyeres leading into the heating-flues; each gas-pipe supplies four lateral flues. The vertical through-going flues, *w*, force the heating-gases to travel within the partition-walls. The air for combustion can be introduced by an opening in front of each gas-burner, where it is forced in by an injector-action of the gas, or else by special flues for each oven (*f*), from the passage L. The heating up takes place by a side valve (v^1), through which the gas enters into the main flue when the valve *v* is shut. Since all the gas-inlets are accessible from below, the heat can be exactly regulated all over the oven, and can, for instance, be increased at the two ends without overheating the oven, which causes a more regular and

quick heating without too much action on the brick-work As the heat is greatest near the bottom, there is no danger of over-

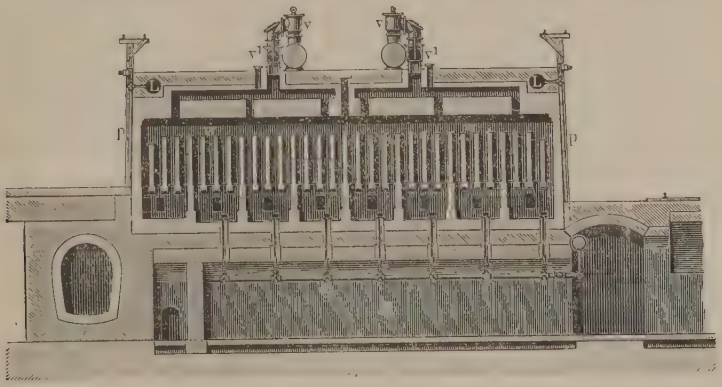


FIG. 9.

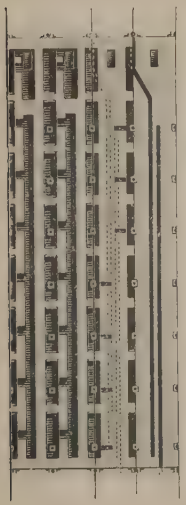


FIG. 10.

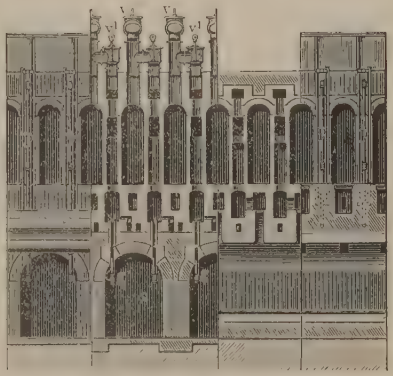


FIG. 11.

heating the gas collected in the upper part of the ovens and thus destroying part of the by-products. The gas-pipe, lying in the foundation, is well protected, and does not interfere with the work on the top of the ovens. The subterranean passages also

serve for heating the air previous to combustion, and thus utilize the heat radiating below. As the heating-gases have a shorter distance to travel than with other systems, there is neither an excessive pressure at their entrance nor a vacuum at their leaving the ovens; hence any leakage of gases into or out of the ovens through joints and crevices is avoided, the quantity of by-products is increased, and the oven-gas is not contaminated with fire-gases. In all these respects the new ovens work better than those provided with recuperators.

A detailed report on the Otto-Hilgenstock ovens, erected at a colliery at Rhenish Prussia, is made by Bertelsmann, in *Z. angew. Chem.*, 1899, p. 1098. There are 30 ovens, with double walls, 33 ft. long, 19·7 in. wide at one end and 23·6 in. at the other (where the coke is drawn). Each charge is about 7 tons of coal, with 14 per cent. water, and requires 30 to 32 hours for finishing. The heating is done by eight Bunsen burners from below; the temperature just above the burners is from 1300 to 1400°. The fire-gases rise perpendicularly and then travel towards the middle, where the temperature is 200 or 300° below the initial one; they are then taken downwards below the bottom of the coking-chamber and are then, with about 1000° C., employed to raise steam in four boilers, producing daily 140 tons steam of 8 atmospheres. The gases evolved in the distillation of the coal are cooled by air and water down to 30° C., washed with weak ammoniacal liquor, deprived of their tar by a Pelouze and Audouin apparatus (p. 33), and by another washing deprived of the last traces of ammonia. They are then collected in a gas-holder from which they are conveyed to the ovens as fuel for these. About 1000 cub. ft. of gas are produced from 100 kg. of dry coal, on an average containing 2·5 CO_2, 3·5 heavy hydrocarbons, 0·8 O, 7·6 CO, 27·2 CH_4, 50 H, 8·4 N per cent. This gas has a fair illuminating power and a heat value of 4300 to 4500 metrical calories.

Several recent patents of the firm C. Otto & Co. contain improvements of the process. Thus, according to Ger. P. 171901, of 1903 (issued in 1906), a saving is effected by shutting off the heating gas from the heating flues entirely or partly before the coking process is finished. Thus only the outside portions of the coal are coked by heat from without, and these coke the inside portions by communicating their heat to them.

Hilgenstock (*J. Gasbeleucht.*, 1902, 617) points out the advantages which the new ovens, fired from underneath, have over the older Otto-Hoffmann and other ovens where the recuperator principle is employed, and in consequence of this the temperature must vary from 1000° to 1300° and backwards, each time the direction of the gases is changed. This must lead to a loss of tar and ammonia, as proved by a number of analyses made of the products of both systems.

A similar combination is the "United-Otto Coke-Oven" (U.S. P. 673928 and 644369), which claims to be the most efficient type of this kind, the coal being handled by machinery from the time it is unloaded from the car into the elevator until it is in the oven, the crushing (where necessary) being done in the same way. The quenching of the coke is also done in an ingenious manner. We must refer for these details (which hardly belong to the scope of this treatise) to a splendidly illustrated treatise on the Destructive Distillation of Bituminous Coal, issued in 1906 by The United Coke and Gas Company, 17 Battery Place, New York.

Short, in *J. Gas Lighting*, 1907, 97, gives a survey of the results obtained with Otto-Hilgenstock ovens, working with Durham coal. We quote from it merely the figures showing how the nitrogen and the sulphur of the raw material appear in the products:—

	Nitrogen, per cent.		Sulphur, per cent.	
Contents of coal	1·57	= 100	0·824	= 100
Left in coke	0·68	= 43·31	0·598	= 72·53
In tar	0·047	= 2·98	0·012	= 1·45
„ ammonia	0·238	= 15·16	as H_2S 0·198	= 24·00
„ cyanides and sulphocyanides	0·0223	= 1·43	other compounds 0·013	= 1·72
„ the gas, and loss		37·12	loss	0·30

A modern Otto coke-oven holds about 7½ tons of coal, which are coked in 36 hours. The yield from Westphalian coal averages 72·2 per cent., so that each oven produces 1100 or 1200 tons of coke per annum (Haarmann, p. 4). The average production in 1900 in Westphalia amounted to 1260 tons per oven from recovery ovens, against only 890 tons from the old open ovens, and in the most modern recovery ovens even 1800 tons are reached (Haarmann, p. 6).

The condensing-plant belonging to the Otto ovens will be described in a later section of this chapter, where also the composition of the gas will be mentioned. In this place we speak only of the composition of the tar.

Tar and *ammoniacal liquor* are separated by settling in large tanks. If the liquor is not strong enough for sale or for working up in the distilling-apparatus, it is used over again in the scrubbers till it comes up to 4° or 5° Twaddell, when it contains about 1·7 to 1·8 per cent. NH_3. Westphalian coal yields about 14 per cent. of liquor at 4°, equivalent to a yield of 1 ton of sulphate of ammonia per 100 tons of dry coal. In the Saarbrücken district the yield is only 14 to 16 cwt., in Lower Silesia 16 to 18 cwt., in Upper Silesia 26 up to 34 cwt. per 100 tons of coal.

The yield of *tar* differs a good deal, according to the quality of the coal and to the efficiency of the cooling-apparatus; it may vary from 2 to 3½ tons per 100 tons of coal.

The following analyses were made in April 1886 of tar obtained from the same coal (A in a gas-works in ordinary retorts, B from a set of Otto's coke-ovens):—

	A. Gas-tar.	B. Coke-oven tar.
Water	2·9	2·2 per cent
Light oil up to 200°	4·0	3·4 „
Benzol for aniline	0·92	1·1 „
Solvent naphtha	0·20	0·32 „
Creosote oil	8·6	14·5 „
Crude naphthalene	7·4	6·7 „
Anthracene oil	17·4	27·3 „
Pure anthracene	0·60	0·70 „
Pitch	58·4	44·3 „
Carbon	15 to 25	5 to 8 „

The expenses incidental to the recovery of the tar and ammonia are not considerable; they consist principally of the cost of pumping the (rather large) quantity of cooling-water, the ammoniacal liquor, etc.; the cost of labour and repairs is very slight.

The following figures respecting the cost of erecting and working the Otto ovens have been supplied to the author by the inventor. The cost of erection naturally varies a good deal according to the situation. On an average it may be taken at

3050 marks (say £150) per oven for the ovens themselves, and 6000 marks (not quite £300) per oven for the very extensive condensing-plant, gasholder, Feldmann's apparatus for ammonium sulphate, etc. This also includes duplicate engines, pumps, and exhausters, and substantial buildings for all these erections.

A battery of 60 ovens converted in six months' time 3073 truck-loads of 10 tons of coal each into coke, and yielded at the same time:—

	Per 100 kg.	
915,245 kg. tar (say, 3 per cent.)	M. 2·30 =	M. 21,050·63
313,446 kg. ammonium sulphate (1·02 per cent.) at	M. 23 =	72,092·58
		M. 93,143·21
Deduct Sulphuric acid 313,446 kg. at 3·80 =	M. 11,910·95	
„ Wages	9,326·26	
„ Salaries	2,936·97	
„ Sundry materials	2,571·50	
		26,745·68
Leaving per 6 months a profit on tar and ammonia		= M. 66,397·53
„ 12 „ „ „		M. 132,795·06
	Or, say,	£6,600.

That is to say, each oven has coked per annum 1020 tons of coal, and the extra profit on tar and ammonia per ton of coal has been M. 2·16 (say 2s. 9d.).

At the Burbacher Hütte in Rhenish Prussia in 1907 a set of 126 of the Otto-Hilgenstock ovens has been erected. The coking takes 36 hours. Tar and ammonia are condensed. The waste heat is utilized for 14 Cornish steam-boilers, with about 1000 sq. ft. heating surface each. The surplus gas, moreover, amounts to between 60 and 90 cbm. per ton of dry coal, according to the amount of water contained in the fresh stock charged. This gas possessing a heat value of about 5000 metric calories per cubic metre. serves for driving a gas-engine of 1200 h.p. for the electric central plant; part of the excess of gas is burned under steam-boilers and serves for driving a gas-turbine of 1200 h.p.

Th. von Bauer, who had suggested to Hoffmann one of the important principles of the above-described ovens, has himself worked out his ideas in a different way, better adapted to the wants of smaller works and to the employment of less bitumin-

ous coals (Ger. P. 28530, 67275, 73701). Since 1887 many hundreds of these ovens have been erected in the Creuzot works, thereby enabling an addition of an equal proportion of anthracite to be made to bituminous coal, whilst formerly only 20 per cent. anthracite could be used. Bauer subsequently worked out his principle in the shape of circular batteries, viz., horizontal ovens for very bituminous coal, half-horizontal for semi-bituminous, and upright for non-bituminous. For the latter the tar and ammonia recovery-plant can be cut off at will, when the first period of work is over. Kassner (*Chem.*

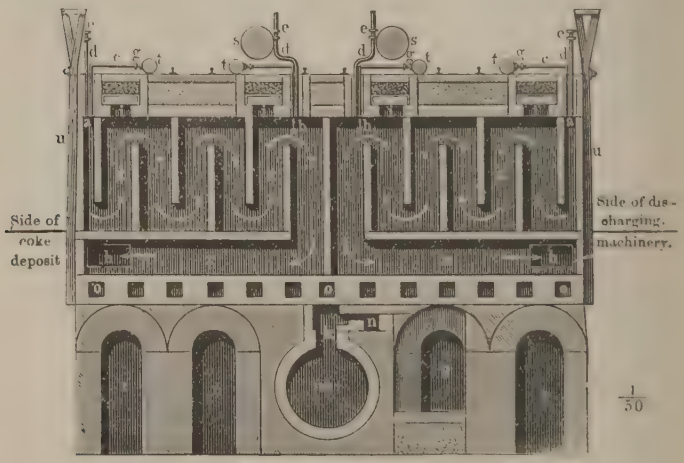


FIG. 12.

Zeit., 1898, p. 993) discusses the results of Bauer's ovens in detail.

Lastly we will describe the oven constructed by J. W. Nienhaus (Ger. P. No. 94016), which aims principally at avoiding an insufficient coking at the ends of the ovens. For this purpose he places the first partition of the heating-flue at the burners *u* on both sides of the oven, Fig. 12, only 8 in. from the ends, whilst the other partitions are 22 in. distant one from another. Thus the fire-gases, before entering the longitudinal walls, first quickly heat the outer ends, and this compensates the loss of heat occurring there by radiation. This also causes

the expansion of the ovens to be quite even, and thus increases their durability. These ovens can also be worked for a considerable time without recovery of the by-products, and yet remain fit to take up the latter at any moment.

Nienhaus contends that in all coke-ovens with vertical flues the upper portion is not sufficiently heated; the charge is more quickly finished below than above, and this has a deteriorating effect on the output and the quality of the product. Nienhaus therefore heats the ovens from above, the gas, as well as the previously heated air, being passed into the various combustion-chambers by tuyeres. (Compare the objections to this arrangement of heating from above, p. 78.) The air for combustion is aspirated by the chimney, and, like the heating-gas, can be regulated by a tap for each chamber, so that the rate of combustion can be checked in all parts of the oven by means of the Orsat testing-apparatus.

III. *Recovery-Ovens on the Modified Carvès System.*

In the introductory part of this chapter (pp. 59 *et seq.*) we have spoken of the former stages of this process, namely, of Knab's, Carvès', Pauwels-Dubochet's, and Pernolet's ovens. Since attention was drawn to the undoubted success of Carvès' ovens, first by Angus Smith, then by H. Simon and others, there have been quite a number of "modifications" of the Carvès' ovens, as Hüssener's, Carvès' own (generally called the Simon-Carvès oven), Ruppert's Semet and Solvay's, Seibel's, the Gottesberg Coal and Coke Company's (*cf.* list of patents, pp. 62 *et seq.*).

Most of these systems have met with only a very restricted application; and we shall confine our description to those which have been more widely introduced, namely, Hüssener's and the "Simon-Carvès" oven, both of them (like some of the others) based upon a previous heating of the air required for combustion (a feature which we have also seen to be the essential point of the Hoffmann-Otto system), and the Semet-Solvay ovens.

The Carvès ovens have been considerably improved by the introduction of recuperators, patented in 1883 (No. 554) by

Henry Simon as a communication from François Carvès.[1] Figs. 13 to 17 show the arrangement Fig. 13 is a longitudinal section through a coking-chamber and cross-section through the external air and smoke-flues on line $\alpha\ \beta$, Fig. 15. Fig. 14 is a longitudinal section through the partition-wall of the coking-chambers on line $\gamma\ \delta$, Fig. 15. Fig. 15 is a part plan and part sectional plan of the coking-chambers and flues. Fig. 16 is part front elevation and part cross-section; Fig. 17 a sectional plan to a smaller scale of the smoke-flues and air-heating flues. We notice the coking-chambers A A (18 to 20 in. wide), the fireplace B with flue C leading thence under the oven floor to the opposite end, where it passes laterally into the flue C_1 in the side wall of the chamber, first rising to the upper part of the wall, then descending in a zigzag direction (Fig. 14), and then down the inclined flue C_2 into the external smoke-flues C_3 C_4. These flues, as will be seen from the plan, Fig. 17, extend along the whole range of the coking-chambers, each flue being closed at one end and communicating with the chimneys D D_1 at the other. The flues C_1 communicate alternately with the flues C_3 C_4, so that the combustion-gases of one half of the range of ovens are discharged into the flue C_3 and those of the other half into C_4, the flow of such gases towards the chimneys D D_1 taking place in contrary directions in the two flues. An air-flue (E) extends first along the outer side of the flue C_4, then runs along at E_1 between the two flues, and, again returning, passes at E_2 along the other side of the flue C_3. From this part of the air-flue, branches E_3 pass off to each coking-chamber, and extend beneath the flue C to the fireplace B, with which they communicate through openings E_4 E_5.

Thus it will be seen that atmospheric air, entering the flue E at E_6, passes along the same in contact with the hot walls of both C_4 and C_3, and lastly through E_2, whence it passes in a highly heated condition through the branch-flues E_3 to the fireplaces of the several ovens, in order to enter there into combustion with the gaseous fuel employed, which, in some cases, may be kept ignited by a small fire of solid fuel on the grate

[1] I take the diagrams in the text partly from the patent, partly from detailed unpublished drawings kindly supplied to me by Mr Henry Simon.

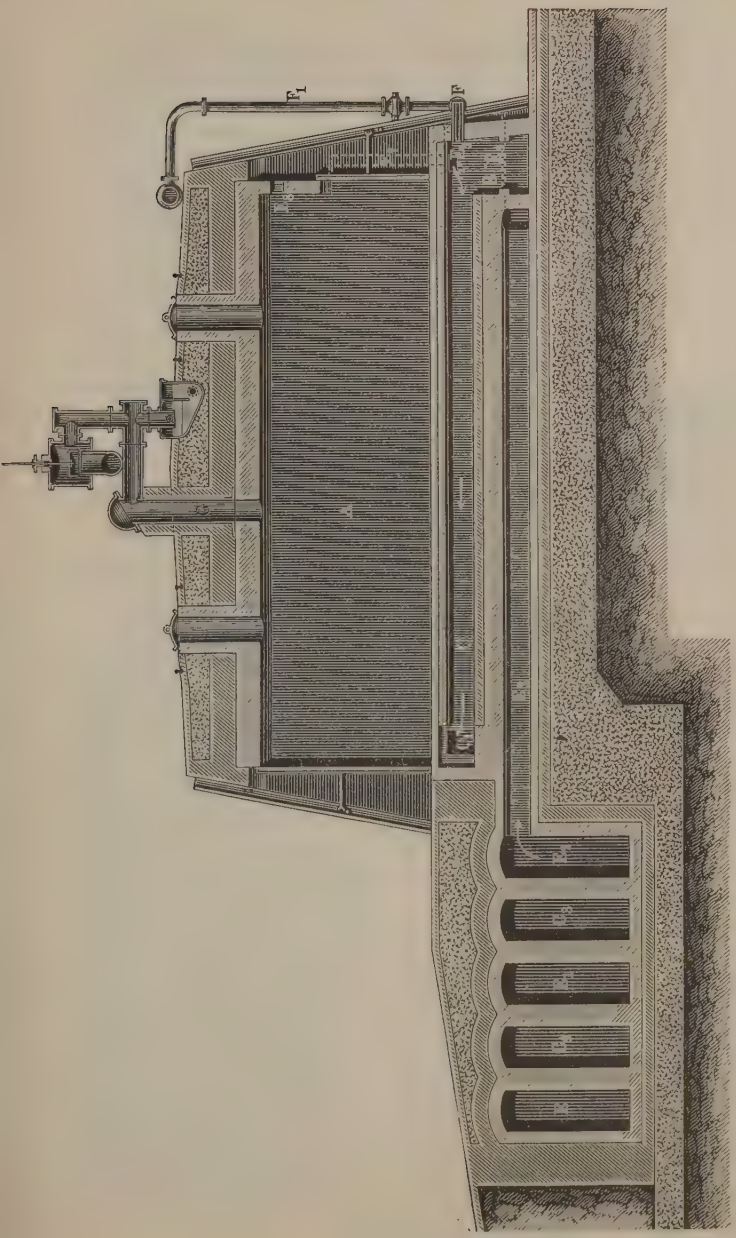


FIG. 13.

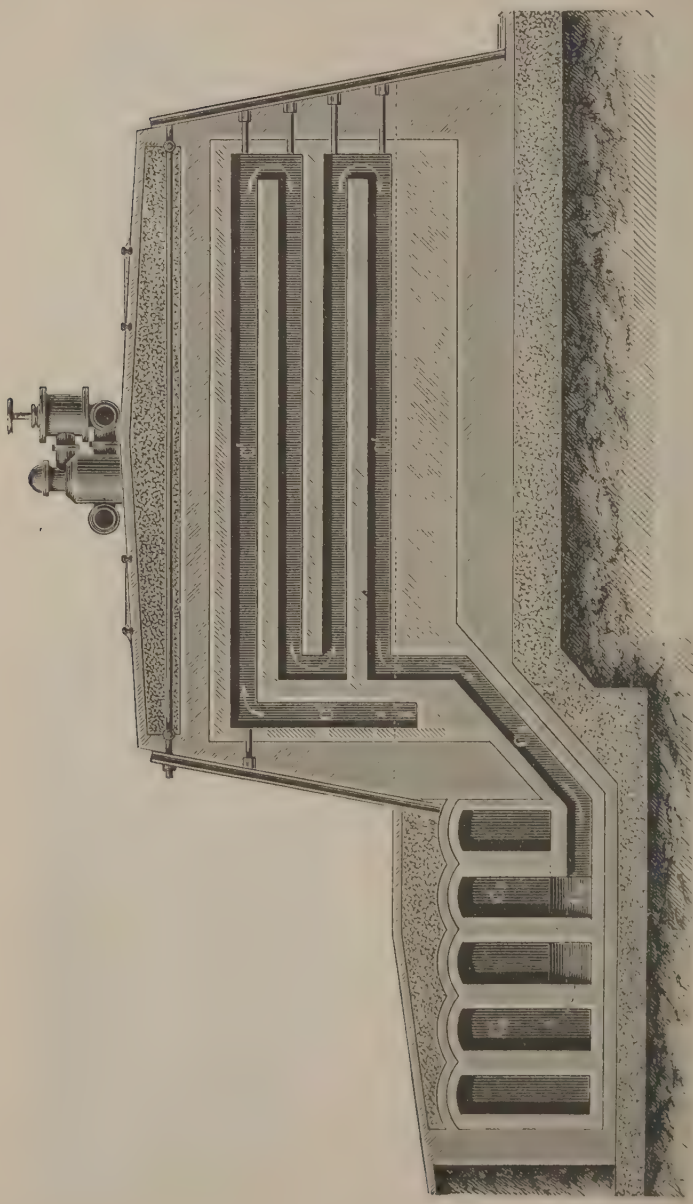


FIG. 14.

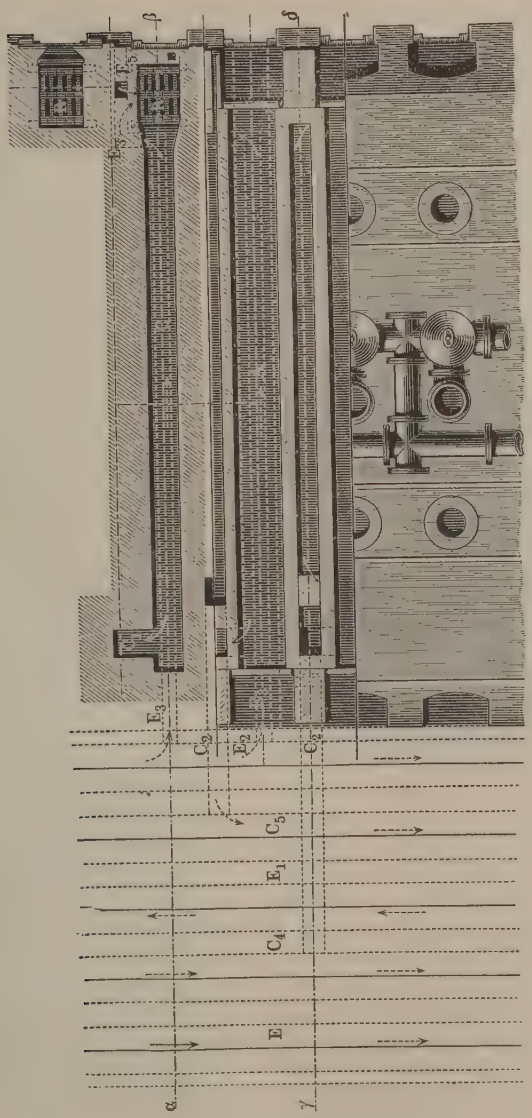


FIG. 15.

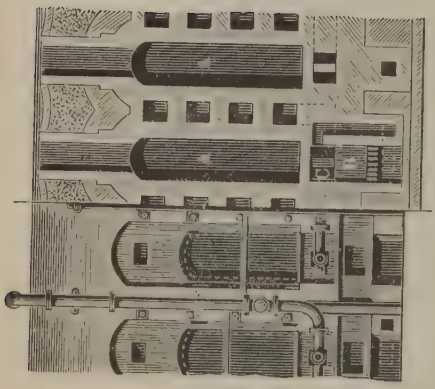


FIG. 16.

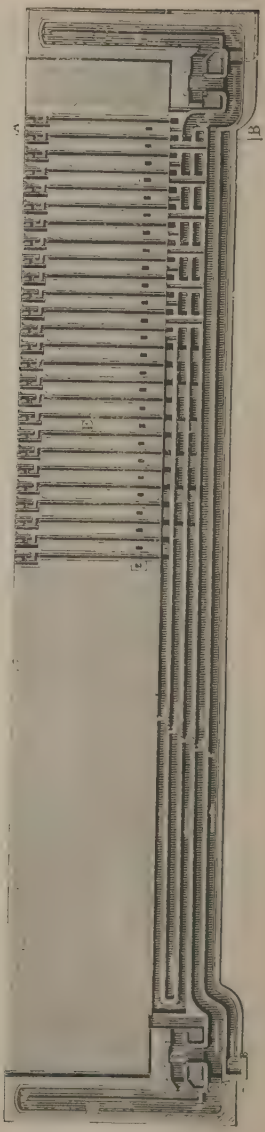


FIG. 17.

shown at B. In E the air flows in the contrary direction to the current of the combustion-gases in C_4, and in E_1 it flows in the contrary direction to that of the gases in C_3, so that the coldest air in each case comes in contact with the cooler part of the smoke-flues, and thus the heat is taken up by the air in the most effective manner. As the air in passing through the flue E E_1 becomes heated to a considerable degree, in passing through the flue E_2 (which is to a very slight extent in contact with the brickwork of the oven) it will not absorb any appreciable amount of heat therefrom, and even this absorption, small as it is, may be entirely avoided by arranging the flues so as not to be in contact with the brickwork of the oven except where they enter it.

The hot air is made to enter the fireplace through the openings E_4 and E_5, the latter being in close proximity to the inlet nozzle F for combustible gas, supplied through the pipe F_1; while the opening E_4 serves to supply air when required to the before-mentioned small fire on the grate. The hot-air flue is also by preference extended up in the front wall of the ovens, as indicated at E_7, in order to communicate at E_8, or at any other convenient point, with the upper part of the flue C_1, so that a portion of the hot air entering there may effect the combustion of any unconsumed combustible gases that may have passed away from the fireplace. The combustible gaseous constituents distilled off from the ovens escape through the flue G, and are led through proper pipes or hydraulic mains to any suitable known apparatus for condensing the tar and removing from the gas other condensable and useful constituents; and the gas, after such purification, is then utilized in whole or in part as fuel for heating the coke-ovens, for which purpose it may either be led directly to the fireplace B, through the pipe F_1 and nozzle F, or it may also be previously heated by first passing it through a pipe or flue situated within or close to the smoke-flues C_4 C_3. As, however, the quantity of gas consumed is small in proportion to the air-supply, the advantage gained in heating it is in most cases not sufficiently great to justify the additional expenditure and greater complication caused by providing apparatus for heating it.

As shown at Fig. 17, the combustion-gases may, before

escaping up the chimneys D, be made to pass through the flues H of steam-boilers or of ovens or kilns or evaporating-pans, in order still further to utilize their heat.

The patent also comprises another modification, in which there is only one external smoke-flue, into which the flues of all the ovens open, and on each side of which there is an air-flue so arranged that the external air passes in the contrary direction to the current of the combustion-gases. In a further modification, instead of having separate air-supply and smoke-flues, the same flues are made to serve alternately for taking up the heat from the combustion-gases and imparting such heat to the air-supply, as in the well-known Siemens's recuperators (such as Hoffmann and Otto employ with the Coppée ovens).

The inventor lays special stress upon his arranging the recuperator-flues externally to the ovens, not inside them; since in the latter case too much heat is abstracted from the ovens, and their temperature is not so high as is desirable for the proper working of the coking-process.

From a paper of Mr H. Simon's[1] it appears that there were then (1885) at work three plants of Simon-Carvès ovens on the new system, comprising 50, 35, and 25 ovens respectively, all of them provided with recuperators. The ovens at Bear-Park are a foot longer than those at Crook, and take a charge of 4½ tons each, which requires rather more than 48 hours to work off, owing to irregularities over night and on Sundays. It is claimed that these ovens are much more substantial than those on the Coppée system, with their extremely thin walls, which are liable to burn away at the intense heat prevailing, whilst it is impossible to inspect them; also that it is most difficult to split up the current of hot gases equally all over the small flues of the Coppée system, and that the gases, rushing through the six-feet length of these vertical flues, have not time to part with their heat, whilst in the Carvès oven the gas has to run more than 100 ft. in one undivided current. Consequently the recuperators in the former system have much more work to do than in the latter. Lastly, it is urged that a continuous process of recuperation must yield more uniform results than one rising and falling with the change of regenerators. The coke from

[1] *J. Iron and Steel Inst.*, No. 1, for 1885.

the new ovens fetches a higher price than any other coke for use in cupola furnaces; so far as blast-furnaces are concerned, there still seemed to be some prejudice in England which had been quite overcome in France, Germany, and Belgium.

The condensing-plant is of a very simple description, but as efficient as could be desired. An attempt to replace rotatory exhausters by Körting's injectors has failed.

From further notes, kindly supplied to the author directly by Mr Henry Simon, it appears that the *yield of coke* is about 77 per cent. in Durham, 69 per cent. in Accrington, 52 per cent. in Staffordshire. The *yield of ammonia*, expressed as sulphate, is 1 per cent. to 1·25 per cent. with North-Country coal, and about 2 per cent. with Staffordshire coal. The *yield of tar* varies from 3 per cent. to 4 per cent., of about 1·1 specific gravity on the average, the quality being equal to any other high-temperature tar. The air is heated in the recuperator to some 430° to 480° C., and the temperature in the various flues is distributed somewhat as follows:—In the top flue C′ (Figs. 15 and 17) it is 1130° to 1180°; in the second flue (where more air is introduced), 1260° to 1278°; in the third flue, 1100° to 1120°; in the lowest side-flue, 1125° to 1130°; in the flues C below the oven-sole, 1540° to 1565° C. Copper may be melted in the top flue, and iron will melt in the flue underneath the oven sole. Only best Dinas bricks can be employed in some of the flues, as the best obtainable material will alone resist such intense heat. The distribution of the heat is very even throughout the sides of each oven, so that the available coking-space is utilized to the fullest extent. The coal is filled nearly to the top of the arch and levelled evenly, even close to the doors; whilst in other ovens, which do not distribute the heat so well, a portion of the space close to the door is lost for carbonizing. It is claimed that, on account of the extreme simplicity of construction, the expense of erecting these ovens is very moderate, and their maintenance is also very inexpensive.

Another modification of Carvès ovens, equally provided with an air-heating apparatus, has been introduced into Germany by A. Hüssener (Ger. P. 16923 and 20196). Hüssener's ovens, of which 100 have been erected in Westphalia, are shown in Figs.

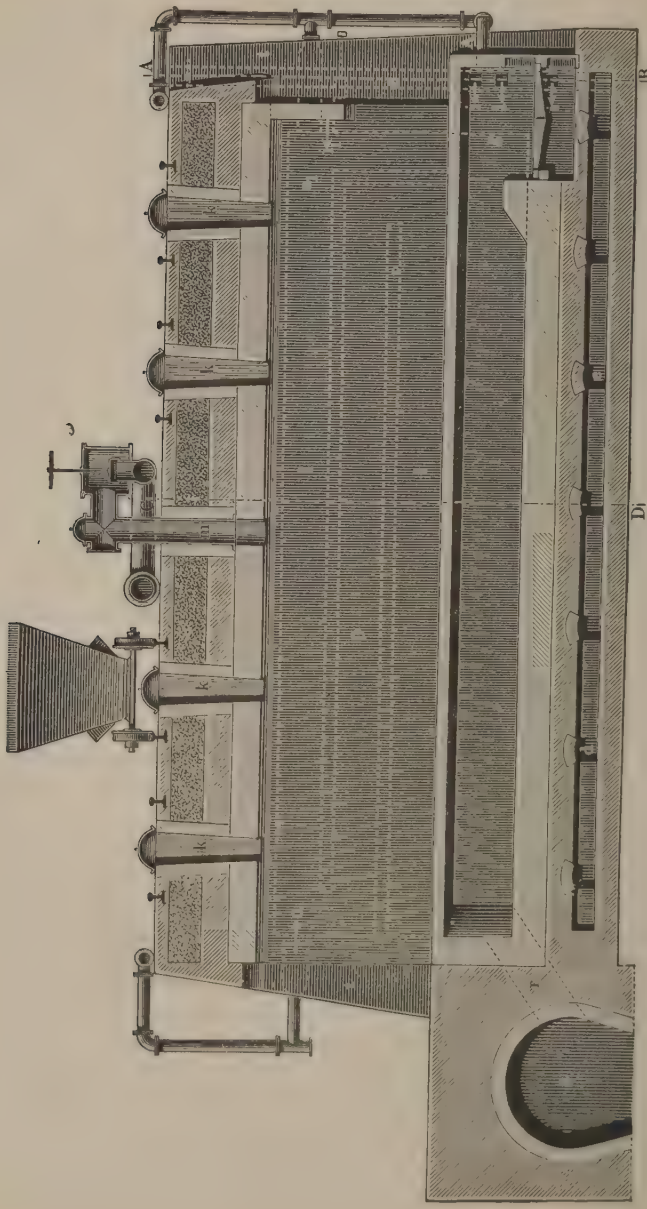


FIG. 18.

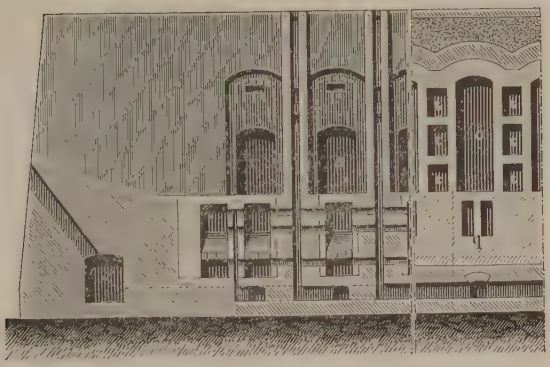


FIG. 19.

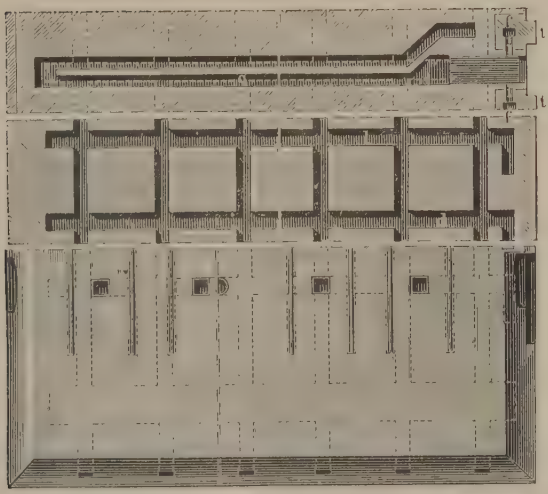


FIG. 20.

18 to 20. Their dimensions are: length 29 ft. $6\frac{3}{8}$ in., width in the middle 1 ft. $10\frac{5}{8}$ in., with a certain taper to facilitate the mechanical pushing out of the charge (as is usual in the case of all horizontal ovens, both those on the Coppée and on the Carvès system); height 5 ft. $10\frac{7}{8}$ in. (the original Carvès ovens at Terre-Noire are 19 ft. $8\frac{1}{4}$ in. × 2 ft. $5\frac{5}{8}$ in. × 4 ft. 9 in.). Their available space is 88 per cent. of the total space, and they take a charge of $5\frac{1}{2}$ tons of finely sifted, dry coking-coal. The charging takes place by four holes (*k k*); the ends are closed by doors turning on hinges; the discharging takes place by the ordinary pushing-out machine (ram). The end walls between the two ovens are strengthened by buttresses (*t*), which at the same time prevent air from entering into the flues. The gases are aspirated by means of an exhauster through the outlet *m*, and are forced through the condensers and scrubbers: they then return to the ovens, and issue by the tube A over the fire-grate *g*, where they take fire. The fire-gases travel round the partition *q*, rise at one end up to the top flue *l*, and descend through the three horizontal flues *l l* and the snore-hole *r* into the main-flue *s*. The mouth of the gas-inlet pipe A is an annular double tube, like a Bunsen burner; whilst the inner tube conveys the air for combustion, the combustible gas issues through the annular space, and both enter at the same time into *g*. Owing to the distance which the products of combustion have to travel before they reach the main-flue *s* (about 100 ft. in a Carvès oven), they were formerly cooled down too much, and the ovens did not get hot enough, whilst the oven bottoms were fluxed. To avoid this, Hüssener introduced a previous heating of the air to about 300° C. in the flues *d e*; it is then conveyed through the small flue *f*, contained in the buttress *t*, partly through *i* in the grate-space *g*, partly through i_1 into the top flue *l*, and in both places gets mixed with gas. This does not seem to have met with complete success; but after adding further gas-inlets at *u* and u_1, the fire on the grate *g* could be left out, the gases sufficing for heating the retorts. [It seems pretty evident that this sort of firing the ovens is not so economical as Otto's; this would also appear from the fact that the Otto ovens have a good deal of gas to spare.]

The cost of erecting a set of 100 Hüssener ovens in

Gelsenkirchen (Westphalia) according to a published balance-sheet, was :—

For utensils	. .	Marks 2,689·33	
„ buildings	. . .	113,225·38	
„ machinery and iron-work	. . .	416,624·43	
„ railway	. . .	38,193·48	
„ well and water-pond	.	30,953·60	
		M. 601,686·22 = per oven, M. 6016·86, or, say, £300.	
„ coke-ovens	. . .	326,475·51 =	3264·75 = £163
„ land	. . .	105,655·15 =	1056·55 = £52
		M. 1,033,816·88 =	M. 10,338·16

Or, say, £50,169 ; per oven, about = £502.

The ovens are charged, at intervals of 60 hours, with 5½ tons of bituminous (proper coking-) coals (say, 700 tons per annum, or two-thirds of the output of the Otto ovens).

They are stated by Hüssener (*Stahl u. Eisen*, 1883, p. 405) to yield :—

	From Gas-coal.	From Coking-coal.
Large coke	61·70	75·00
Small coke	3·60	0·80
Coke-breeze . . .	9·18	1·20
Tar	2·72	2·77
Sulphate of ammonia . .	0·924	1·10

The ammoniacal liquor has 5° Tw. and contains 1·65 per cent. NH_3. The tar is very thin ; its specific gravity differs but little from that of the ammoniacal liquor. According to analysis made in November 1882, it yielded :—

58·83 per cent.	distillate .	0·59	benzol 83-100° C.
39·51 „	pitch . .	0·49	„ 100-140° C.
1·66 „	loss . . .	0·39	solvent naphtha.
		1·37	pure phenol.
		0·95	pure anthracene.

The yield of phenol and anthracene is much higher than from ordinary gas-tar.

The *Semet-Solvay oven*, which is also an outcome of the Carvès principle, is extensively used, especially in Belgium and France. We give the following description of this oven, as erected at the Havré colliery near Mons (Belgium), according to communications from M. Demanet, manager.

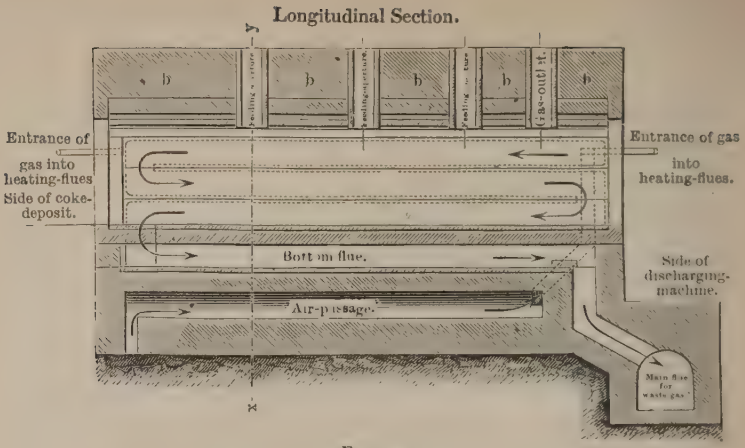


FIG. 21.

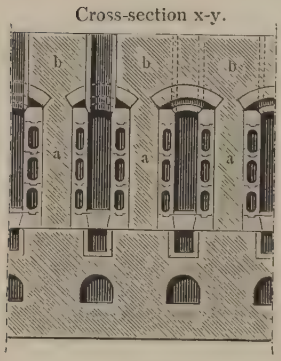


FIG. 22.

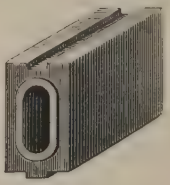


FIG. 23.

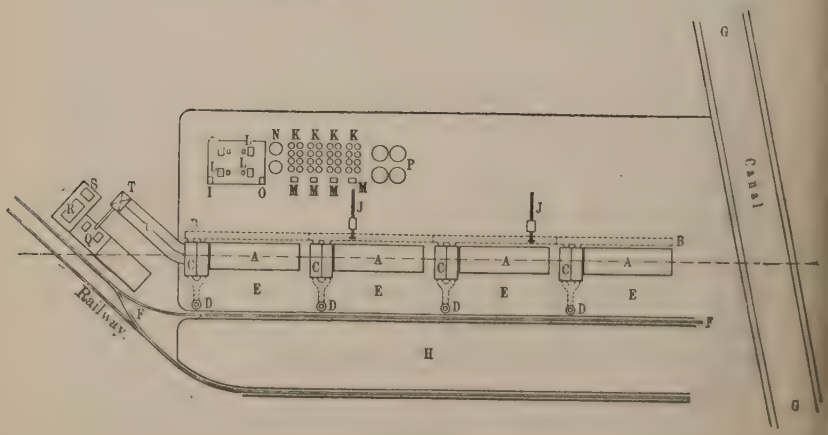


FIG. 24.

The oven is 29 ft. 6 in. long, 5 ft. 7 in. high, 14·2 in. wide at one end, and 14·96 in. wide at the other (where the coke is pushed out). The heating-flues, where the gases are burnt, are built independently of the partitions between the ovens, and are therefore easily renewed without injury to the ovens themselves. They are formed of thin-walled, retort-shaped pieces (Fig. 23), fitted into each other by rebates, and thus joining tightly. This construction, whilst strong, admits of rapid transmission of the heat through the thin walls, and thus of quick work; and at the same time it reduces to a minimum the communication between the flue-gases and the vapours formed inside the ovens, which is very important for the yield of by-products.

Two forms of these retort-shaped flue-pieces are in use. One of these has three planes, the fourth being formed by the brick-work of the partitions; the other possesses four planes (Fig. 23), which is more expensive, but affords better protection for the partitions against the heat. Experience has not yet shown which is preferable. The partitions are made two bricks thick; the walls of the retort-shaped flues are only 2·36 to 2·75 in. thick.

In order to keep the heat together as much as possible, the top arches are 3 ft. 11 in. thick, and all cast-iron doors are provided with sheet-iron outer doors.

Formerly small heating-flues were provided underneath the floors of the ovens, which were believed to be absolutely necessary for dry coals. Now, however, these are dispensed with, and the fire-gases are driven from the top downward, as shown in Fig. 22. A portion of these gases issues on that side of the ovens where the coke is discharged, and passes into the *upper* row of heating-flues, along the middle and bottom rows, and ultimately through the flue beneath the floor. A second supply of gas circulates on the opposite side of the oven into the *middle* row of flues. This arrangement avoids the formation of explosive mixtures and distributes the heat equally.

The air required for burning the gas is aspirated by a chimney, and is heated in a flue, situated below the hot oven-bottom, to 200° or 300°, before it issues into the heating-flue, where the gases are first introduced. This produces complete combustion and intense heat, and does away with the small fires formerly used for heating the oven-bottoms, so that at present only half the gases produced by the distillation of the coals are

required for the coking-process, although the coal contains only 16 or 17 per cent. volatile constituents. The other half of the gases is utilized for steam-production, and the excess allowed to escape into the atmosphere. Much more steam is produced than the works can utilize, and the excess of steam is passed over to neighbouring ammonia and alkali works. We can to some extent estimate the degree of utilization of the gases, when we consider that 4·5 per cent. water of the weight of coal and 1·5 per cent. tar is condensed, together 6 per cent., before the gas is passed into the heating-flues; thus leaving 10 or 11 per cent. for performing the coking process, only half of which is actually needed.

This utilization of gases is accomplished only by carefully preventing the entrance of air into the ovens. All doors are provided with asbestos-lined joints, and all the joints of the charging-holes, peep-holes, etc., are carefully faced, so that they close tightly by means of springs, and the luting with clay (always unreliable) is dispensed with. The air-tightness of the ovens is proved by the fact that the coke, when discharged, does not show any sign of combustion.

The gas is distributed in the heating-flues under uniform pressure by means of pipes of exactly the same section, so that all ovens receive an equal quantity of gas, and the draught from each oven into the main outlet-flue is also regulated by means of dampers, so as to be equal for all ovens. Hence the work can be regulated at one and the same time for all ovens by means of the chimney-damper. When entering the chimney, the temperature of the gas is scarcely 200° C.

At Havré four sets (A) of 25 ovens each (Fig. 24) are in use, every one of which consumes from 100 to 110 tons per day. The waste heat of the whole battery is passed, by subterranean flues (B B), underneath the steam-boilers C; the gas at last issues into the chimney D. Each set of ovens heats two steam-boilers of 800 superficial feet heating-surface. The chimneys are 82 ft. high and 5 ft. 3 in. wide.

E is the coke-pit, made of cast-iron plates, situated above the railway F running to the canal G G. The coke is pushed out by means of the steam-ram I.

The gases and vapours produced in distilling the coal are aspirated by the exhausters L, and first cooled in tanks on the

top of the ovens by means of cold water, so as to avoid any stoppage further on through the deposition of thick tar. They then pass through the condensers K and scrubbers M, and ultimately through tuyeres into the heating flues. Each set of 25 ovens is provided with a Beale exhauster, capable of aspirating 35,000 cubic metres per 24 hours, and adjustable for the process in each set.

The scrubbers (M) have each seven perforated sheet-iron shelves. N are tanks for ammoniacal liquor and tar; O is a pump connected with the reservoirs P, placed at such an elevation as to facilitate shipment into cistern-wagons.

The cost of an oven is 4600 fr., that of the condensing-plant 1600 fr. per oven; altogether, 6200 fr. per oven.

Each oven is charged with 4 tons of coal, which requires, on an average, 22 hours for distilling. A 25-oven battery finishes 25 charges per day. The yield is equal to that required theoretically, viz., with coal of 16 to 17 per cent. volatile constituents, 81 or 82 per cent. coke. As by-products are obtained 6 or 7 kg. sulphate of ammonia and 14 or 15 kg. tar per ton. Wages and repairs are slightly higher than without recovery of by-products—say 0·30 fr. per ton; but the wages do not exceed 1·30 fr. per ton, and as the profit on by-products is = 1·80 fr., the clear profit is 1·50 fr. per ton. Now an old coke-oven, without recovery-plant, costs 2000 fr., and produces 60 tons coke per month, or 3300 fr. for 100 tons per month; a Semet-Solvay plant for the same production costs 6200 fr. or 2900 fr. more. But the extra profit on these 100 tons being 150 fr. per month, or 1800 fr. per year, the additional outlay bears interest at the rate of 60 per cent. per annum.

At the Phœnix Iron Works at Laar (Rhenish Prussia)[1] each Semet-Solvay oven consumes 1643 tons of coal and yields 1273 tons coke per annum. The yield from 1000 kg. of dry coal is 775 kg. coke, 10 kg. tar, 7·6 sulphate of ammonia. The thick arch accumulates the heat, and admits of keeping the ovens hotter than any other system, so that, without recuperators or air-heaters, it is possible to mix from 73 to 77 parts of bituminous coal with 29 to 27 parts of dry coal, and to obtain excellent coke, but of course lessl tar and ammonia than without the addition of dry coal.

[1] *Chem. Ind.*, 1893, p. 338.

We must not omit to mention that Hüssener does not admit these advantages of the Semet-Solvay ovens; but then we must bear in mind that he is the inventor of a competing system (pp. 91 *et seq.*).

The following comparison of Semet-Solvay ovens in use at the present time at Syracuse, N. Y., and beehive-ovens is quoted from *Stahl. u. Eisen*, 1895, p. 1070:—

	Semet-Solvay.	Beehive.
Number of ovens	12	12
Average time of coking . . . hours	20	51½
Number of ovens discharged in 24 hours	14·4	5·5
Coal coked in 24 hours . . . kg.	71,688	27,760
Coke produced in 24 hours . . . kg.	57,669	17,327
Sulphate of ammonia produced in 24 hours, kg.	772	nil
Tar produced in 24 hours . . . kg.	2651	nil
Yield of coke per cent.	80·7	62·3
„ sulphate of ammonia	1·075	nil
„ tar	3·69	nil
Value of coke made in 24 hours (marks)	402·70	120·08
„ sulphate of ammonia do. (do.)	214·28	nil
„ tar do. (do.)	122·72	nil
	740·00	120·08
Value of products from 1000 kg. coal	61·65	10·00
Cost of each oven (marks)	6400	1260
Duration „ (years)	10	5
Quantity of coke made in each oven (kg.)	17,638	2957
Cost of oven per 1000 kg. coke (mark)	0·35	0·46

In 1899 there existed in Belgium 579, in Great Britain 370, in the United States 297, in France 155, in Germany 97, in Japan 16 Semet-Solvay ovens, altogether 1514, with an aggregate production of about 1,720,000 tons of coke (J. H. Darby *Stahl. u. Eisen*, 1899, p. 1055.

According to *Eng. and Min. J.*, 1899, p. 424, the Semet-Solvay ovens at an English colliery furnished from 100 tons of coal: 70 tons coke, 4¾ tons tar, 1½ tons sulphate of ammonia—303 gall. crude benzol, and the equivalent of 13 tons steam. At the prices of that time the recovery of the by-products yielded a profit of 50 per cent. on the expense connected therewith.

A coke-oven of the upright type is that of R. Barlen (Ger. P. 183670) who claims that the by-products are better protected against decomposition than previously, and that the coking pro-

cess goes on more quickly and uniformly. By means of a set of Bunsen burners the sides of the coking chambers are heated quite uniformly in the horizontal direction, but more and more strongly from the top downwards, the burners being arranged all over the side of the chambers from the top downwards, and the flues for the combustion gases in the same way.

Lastly, we will enumerate a number of recent patents for by-product coke ovens:—

Wechselmann, Ger. P. 103508.
Festner and Hoffmann, Ger. P. 103577.
Dillon de Micheroux, Ger. P. 104864.
F. Otto & Co., Ger. Ps. 105432, 106959, 171901, 171203.
Coppée, Fr. P. 290799.
Gewerkschaft König Ludwig, Fr. P. 289213.
Hilgenstock, B. P. 19757, of 1899.
Schniewindt, Belg. P. 143472.
Brunck, Ger. P., 20th January 1899.
Rigby, B. P. 20716, of 1901.
Holmes, B. P. 25493, of 1901.
Audonin, Aus. P., class 26, No. 9101.
Heinemann, Ger. P., 138250.
Scheibe, Ger. P. 184038.
Henz, Ger. P. 183823.
Von Bauer, Ger. P., appl. B36982.
Burgemeister, Ger. P. 154028.
Everitt, B. P. 13316, 1904.

Russig, in *Chem. Zeit.*, 1901, 478, reports on new processes in the industry of coke. Poetter & Co., of Dartmund, heat the coke-ovens from above in a special manner, to lessen the speed of the heating-gases and get more equalized results.

C. Schmidt and J. Chasseur, of Mülheim a. d. Ruhr, avoid the drawback of unequal suction from the various ovens of a set by means of a receiver, provided with subdivisions, luted by the tar, the aspiration taking place through side-channels in these divisions.

The Universal Fuel Company of Chicago surrounds the coking-chambers with a brick grating, which is heated to a white heat by the flame and produces a very uniform heating.

Koppers (U.S. P. 862976) cools the gases approximately to the due point of water, passes them through a separator where

the tar floating as mist in the gases is withdrawn from them, superheats them again and condenses the ammonia in an acid bath, kept at a uniform concentration.

Heinemann (Ger. P. 138250), Weissbein (Ger. P. 144148), Collin (Ger. Ps. 138622 and 144828), Cunow (Ger. P. 143307), describe other improvements in recovery coke-ovens (Fischer, *loc. cit.*, pp. 19 *et seq.*

Picák (Aus. P. appl. A7292, 6th December 1906, *Chem. Zeit. Rep.*, 1908, p. 4) takes tar and ammonia out of the gases from the destructive distillation of coal, etc., by the liquid, kept in constant circulation between the scrubbers and the ammonia still, the latter being at the same time heated by these gases.

Condensing Plant for Tar and Ammonia connected with Coke-ovens.

The *condensing-plant belonging to the Otto ovens* is shown in Fig. 25. The gas is first passed through the tube *t* and cooled by upright wrought-iron cylinders or towers, A A. Within the cylinders are a number of iron tubes, fixed in partitions at top and bottom. The top partition forms a water-trough, constantly fed with cold water, which flows downward through the tubes into the bottom box, and thence away into the next tower. The towers are so connected that the cooling-water used in one of them is taken up to a second tower, and so on. The gas travels exactly in the opposite way in the space between the cooling pipes, entering at the bottom and issuing at the top, and is thus cooled. The temperature of the gas in the tubes *i i* (Fig. 6, p. 73), rising from the ovens, is 600° to 700° C., in the main receiver, *l*, 200° to 400° (according to the distance from the tubes *i i*), in front of the gas-coolers 75° to 120°, after passing through them 17° to 30°. In the coolers A A (Fig. 25) it loses a good deal of its tar and about 75 per cent. of its ammonia, in the shape of ammoniacal liquor. The quantity of cooling-water required is about 5 tons per oven in 24 hours.

The gas is aspirated from the coolers A A by means of blowers B B, and is forced into the scrubbers C C. These are upright wrought-iron cylinders or towers containing a large number of perforated iron shelves, 4 inches apart; water trickles down through these, whilst the gas travels from the bottom

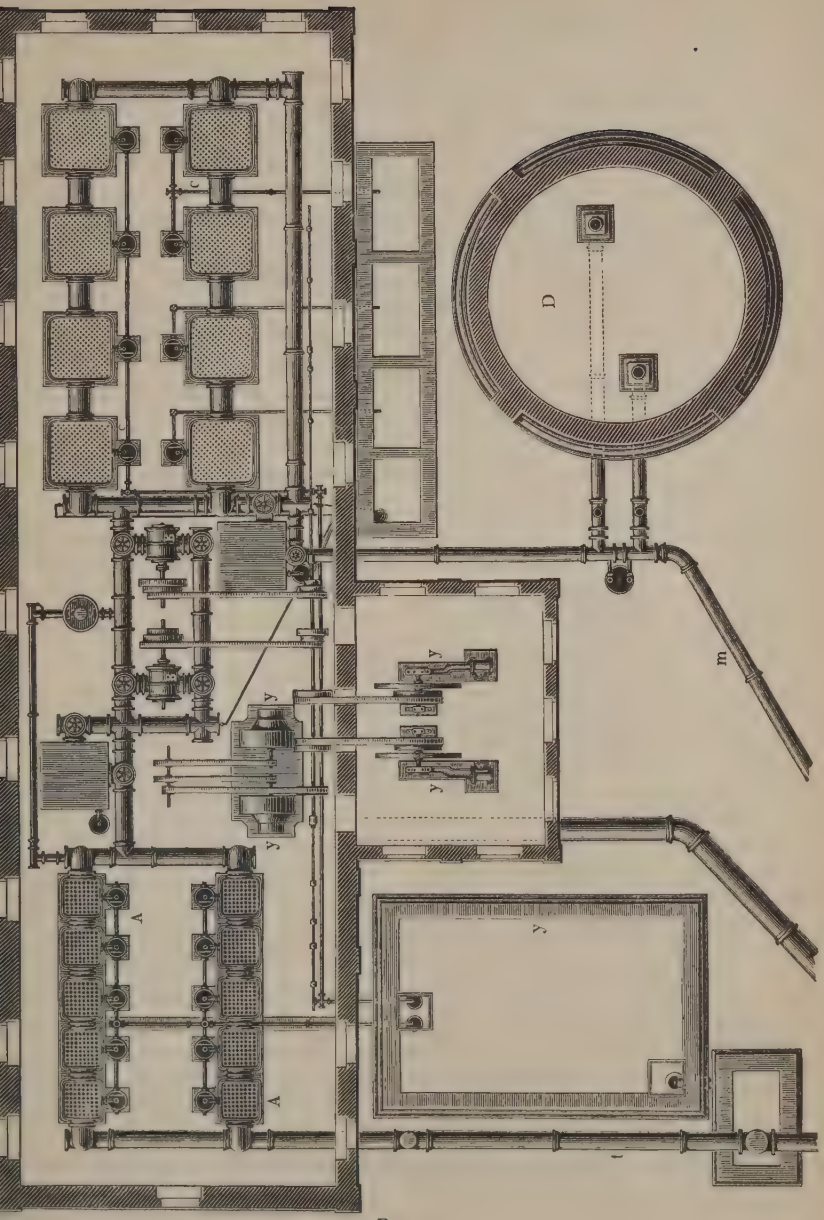


FIG. 25.

upwards. The ammonia is thus washed out; the liquor runs off at the bottom, and is, in case of need, pumped up over and over again, till it is strong enough for sale. Several scrubbers are connected in such a way that the gas at first passes through that containing the strongest liquor, and at last that fed with fresh water. Along with the remaining 25 per cent. of ammonia, the scrubbers also produce a good deal of tar. The temperature of the gas, which is now returned to the ovens, is 13° C. Since a large quantity of gas cannot be burned in the ovens, as it would produce too much heat (as mentioned above), the excess is stored in a gas-holder (D), and can be used for illuminating, for heating steam-boilers, or other purposes. The gas-holder also acts a very important part in equalizing the pressure, and in preventing any damage from chance explosions, in which case only water would be driven out from underneath the gas-holder.

The composition of this gas in a special case (the Pluto-pit ovens) was :—

	Moist, per cent. by vol.	Dry, per cent. by vol.
Benzene vapours, C_6H_6	0·60	0·61
Ethylene, C_2H_4	1·61	1·63
Sulphuretted hydrogen, H_2S	0·42	0·43
Carbon dioxide, CO_2	1·39	1·41
Carbon monoxide, CO	6·41	6·49
Hydrogen, H	52·69	53·32
Methane, CH_4	35·67	36·11
Water	1·21	...
	100·00	100·00

Such gas has about half the illuminating-power of ordinary, retort-made coal-gas, and it can be used for lighting purposes by employing sufficiently large burners. In Westphalia it is employed for heating steam-boilers, along with the waste heat of the gases issuing from the recuperators into the chimney (420° C.).

A recent German patent of the firm C. Otto & Co. (No. 171203, of 1903, issued in 1905) prescribes conveying both all the tar and the ammoniacal liquor, beginning from a certain point back to the main receiver. The gaseous current thus established between the gases from the main and the condensater running back yields a product very rich in ammonia and benzol.

According to their Ger. P. 174695 (of 1902, issued in 1906), the ammoniacal liquor obtained according to the preceding patent is cooled and then employed for washing the ammonia out of the gases.

A detailed description of condensing plant placed at my disposal by Mr Ernst Henss, of Nied am Main, of a condensing plant attached to a set of Otto coke-ovens, which in 27 hours treat about 250 tons of coal, containing 10 per cent. of water. This plant consists of the following parts:—

(*a*) 1 Receiver at the ovens.
(*b*) 2 air-coolers with tar syphons.
(*c*) 2 tubular water-coolers.
(*d*) 2 high-pressure gas exhausters.
(*e*) 2 horizontal steam engines.
(*f*) 6 tar and ammoniacal liquor pumps.
(*g*) 4 centrifugal water pumps.
(*h*) 1 tar separator.
(*i*) 1 tubular cooler for the last cooling of the gas.
(*k*) 2 ammonia scrubbers.
(*l*) 1 water separator.
(*m*) 2 benzol washers.
(*n*) 1 separator for the washing oils.
(*o*) 3 pumps for the same.
(*p*) 1 flushing cooler for ammoniacal liquor.
(*q*) 1 cooler for the heated cooling-water.
Tanks, pits, connecting pipes, shafting, etc.

The gas (about 9000 to 10,000 cub. ft. per ton of coal) leaves the ovens at the top through a rising pipe which, by means of a valve, dips into the semi-cylindrical iron receiver common to the whole set of ovens. The temperature of the gases on leaving the ovens is from 300° to 360° C., and it enters into the receiver with about 200° to 250° C. This reduction of temperature causes a condensation of the more highly boiling portions of the tar, together with most of the mechanically carried away coal-dust into "thick tar," a semi-fluid tar of low value accompanied by a little thin tar and ammoniacal liquor containing mostly fixed ammonia salts. Some "thick tar" also accumulates in the pipes rising from the receiver and in the valves belonging thereto. In all these parts of the apparatus (in the receiver itself in distances of about 3 ft. from one another)

cleaning-holes, easily closed by caps, must be provided, through which iron poles can be introduced for detaching the tar from the walls of the apparatus, and moving it forward to the "explosion-pit," connected with the main by a somewhat steeply inclined gas-pipe which descends into this pit and dips underneath the liquid. In this pit, made of brickwork and iron, the tar and ammoniacal liquor condensed up to this point are collected, and it serves at the same time as a safety factor; for in case of the gases in the main taking fire, no explosion can propagate itself into the subsequent parts of the condensing-plant, the gases getting vent in the "explosion-pit" by means of an outlet pipe, dipping into the tar and passing outside. In order to prevent such combustions and explosions as much as possible, the caps belonging to the cleaning-holes (*v. supra*) must be put on again immediately after use. The thin tar and ammoniacal liquor are run off the surface of the thick tar in the explosion-pit, and the thick tar is from time to time removed by means of iron rods.

It is not advisable to cool the gases too suddenly, as this gives rise to troubles through plugs of naphthalene forming in the pipes and valves.

From the explosion-pit the gases pass into the air-coolers (*b*), where the remaining portions of thick tar are condensed, together with a good deal of thin tar and of ammoniacal liquor, and are removed by means of syphon traps. There are two air-coolers, in the shape of upright wrought-iron boxes, about 7 ft. wide, and 33 ft. high, with a partition in the middle not reaching quite to the top, so that the gases ascend in one half and descend in the other half, the inlets and outlets being both near the bottom. From here the gases pass into the tubular water-coolers (*c*). These are perpendicular wrought-iron cylinders, 8 ft. diameter and 30 ft. high, with false bottoms into which wrought-iron pipes of 4 in. width are fitted. Through these pipes cold water is flowing: the gases are carried in the space between them, upwards and downwards, by means of partitions, in a current opposite to that of the cooling water. The liquids condensed during this passage pass through hydraulically-luted pots into the pit, where tar and weak ammoniacal liquor are collected. The hydraulic lutes must be made to correspond with the vacuum, produced by the ex-

hausters (*e*), placed at this point, which force the gases to the parts of the apparatus following behind them. The vacuum, beginning at the receiver (*a*), naturally decreases later on, and thus varies from 0 to 200 mm., the pressure on the other side being from 300 to 250 mm. of mercury. Corresponding to this, the hydraulic seals must be at least 500 mm. deep.

On the other side of the pumps the gases are brought under a pressure of 250 to 300 mm. in order to drive them through the tar-separator, the after-cooler, the benzol and ammonia-washers, back into the coke-ovens; on entering these the pressure should be still about 50 mm. This is necessary in order to prevent explosions in the gas conduits, which must happen if there was a vacuum at this point at which air would enter into the gas conduits, instead of doing so only in the flues round the coke-ovens. Such explosions have sometimes taken place when new plants were being started, during which time consequently special care must be taken. Otherwise they may happen when the engine or the pump suddenly break down, or an accidental vacuum is caused by faults in the joints, etc. In such cases they can still be prevented by stopping the conduit in front of the ovens by means of a slide provided for that purpose.

The quantity of cooling-water should be regulated in such manner that it leaves the system at a temperature of 70° to 80°, the gases being cooled down ultimately to 25° to 30° C., but this is mostly attained only in the second cooler behind the pumps. The heated water is usually cooled down by flowing down over large surfaces and here meeting a current of air; it can be brought down to 17° or 18° and used over again for the water-coolers.

An exhauster forcing 100,000 cub. ft. of gas per hour against a total pressure of 3 ft. requires 17 or 18 h.p., with 80 revolutions per minute. They are now constructed up to pumping 300,000 ft. of gas per hour. Most coke-works require only three such pumps, two for actual work and a third as reserve in the case of a breakdown. The driving-engine, whether steam-engine or electromotor, should also be provided in duplicate. Of course pressure-gauges are provided in suitable places, as well as peep-holes and small taps for lighting the sample of gas issuing from them, the length of the flame (about 6 in.) and

its vibrations serving as a good control for the working of the system.

All portions of the system must possess outlets for the condensed tar and liquor towards the great covered pit where these separate.

Behind the exhausters (*l*) we find first a tar separator (*h*), usually constructed on the principle of Pelouze and Andouin, as described on pp. 33 *et seq.*, viz., containing a series of perforated plates, the holes in each plate corresponding to a full place above and below, so that the gases are subjected to continuous shocks against solid surfaces, by which the foggy particles of tar are united into larger drops, flowing downwards. Then comes a tubular water-fed cooler (*i*), by which the temperature of the gases should be brought down to 20° to 25° C. The cooling-water is brought back to 17° or 18° C. by means of the cooler (*g*), which is a mass of thorns and works on the "graduating" principle.

The cooled gases now pass into the ammonia scrubbers (R), cylinders of from 7 to 13 ft. diameter and 25 to 50 ft. high, filled with a large number of wooden sieves, and fed with a well-distributed quantity of water. When leaving the second scrubber, the gas ought not to contain more than traces of NH_3, say, not above 5 g. NH_3 to 100 cbm., but sometimes this goes down to 2 or 3 g. The liquor produced in the second scrubber, containing 4 to 6 g. NH_3 per litre, comes up to 0·6 up to 1·5 per cent. NH_3, and is used for feeding the first scrubber, where it comes up to the proper strength and is then sent to the ammonia works. The gases pass from the second absorber through the water-separator (*l*), and then to the benzol condensers (*m*), which are built exactly like the ammonia washers, but fed with tar-oil (*cf.* pp. 43, 47), being equally followed by an oil-separator (*n*). Generally, about 85 to 90 per cent. of the benzol contained in the gases is recovered here. The residual gas now passes on to the coke-ovens, where it serves as fuel.

The yield of tar from good coking-coal averages 2½ to 3½ per cent., that of ammonia (calculated as sulphate) 1 per cent.

Improvements in the condensing-plant of by-product coke-ovens are described by Brunck (Ger. P. 137563), in order to recover the vapours formed during the drawing and charging of

the ovens, where the principal gas-conductors are shut off by means of a special gas conduit. (*Fischer's Jahresber.*, 1903, p. 17.)

Quality of the Tar produced in various Forms of Coke-ovens.

We have already partially treated of this subject in connection with the gas industry, pp. 30 *et seq.* It has been extensively treated by Watson Smith, whose communications will be found in *J. Soc. Chem. Ind.*, 1883, pp. 403, 495; 1884, pp. 9, 64; and 1885, p. 451. We must refer for details to those papers, and here give only a short abstract of their contents.

The tar or tar-oil from *Jameson's coke-ovens* (p. 66) has a specific gravity of 0·960 to 0·994. It contains no benzene, but very little toluene and rather more xylene. The largest proportion consists of oils boiling between 250° and 350° C., evidently belonging to the marsh-gas series; they are of little value for burning, and of but secondary value as lubricants. From the higher boiling-oils (up to the point at which pitch remains in the retort) a small quantity of paraffin, melting at 58°, separates. By treating the crude oils with caustic soda a fair amount of phenols was extracted; but they contained no carbolic acid, by far the largest proportion distilling between 235° and 300°, and they appear to resemble the complicated phenols found in wood-tar creosote. Neither naphthalene nor anthracene is present. Altogether the Jameson tar evidently belongs to the class of tars obtained by the distillation of coal at lower temperatures, and cannot be classed with the ordinary gas-tar. Watson Smith considers it an excellent material for creosoting timber. The results of Watson Smith entirely coincide with those obtained in 1873 by Behrens with the tar from Pauwels' coke-ovens (p. 59).

H. E. Armstrong (*J. Soc. Chem. Ind.*, 1885, p. 451) expresses the opinion that the Jameson tar or oil might be improved by passing it through red-hot retorts, and is thus "intrinsically" more valuable than the tar from closed coke-ovens. This idea, as well as his opinion that the construction of the beehive or the Jameson ovens more nearly approaches the ideal of a coke-oven than the closed ovens of Carvès and others, is directly

opposed to my opinion, and probably to that of most competent observers. Mr Watson Smith, who had already in 1883 conceived the plan of treating the Jameson oils as suggested by Armstrong, and who was on the point of patenting it but relinquished this plan, states, as his reason for doing so, that the expense and losses of this process are ruinous unless these oils are to be had for almost nothing; and I entirely agree with that opinion.

A later analysis of another sample of Jameson tar by Watson Smith (*Industries*, 1886, p. 162) has in every way confirmed the conclusions formerly arrived at.

The tar from the *Simon-Carvès ovens* (p. 86), as produced from Pease's West coals, is black and thick, of specific gravity 1·106, and closely resembles the tar produced in the London gas-works, in containing very much naphthalene and anthracene, but less benzene, toluene, xylene, and carbolic acid than Lancashire tars. Paraffin is altogether absent. A fractional distillation of 2400 c.c. yielded:—

Below 120°	6·2	per cent. by vol.	water.
„ 120°	1·6	„ „	naphtha.
„ 210°	2·9	„ „	oil.
„ 220°	1·3	„ „	„
„ 230°	0·5	Nearly all solid naphthalene.	
„ 300°	18·6	Naphthalene and anthracene, mixed with intermediate oils.	
Above 300°	34·2	Nearly all solid crude anthracene; little red oil.	
Residue	30·5	per cent. by weight	half-coked pitch.

The pitch-coke was saturated with ammonia.

A determination of the real anthracene by Luck's method yielded 0·73 per cent., comparatively a very large amount, but if any considerable quantity of paraffin is contained in such tars (it was stated to be altogether absent in the above case; see, however, below), this would make it useless for the manufacture of alizarine. The benzene seems to be very rich in thiophene.

An analysis of the Simon-Carvès tar from Pease's West, by S. A. Sadler, yielded 4·5 per cent. by volume of light oils, 20·4 per cent. by volume of creosote oils, with much naphthalene,

and 34·2 per cent. of thick anthracene oil. Further treatment of the distillates gave :—

	Per cent. on tar.
Water	10·00
Benzol, 50/90 per cent.	0·50
Solvent naphtha (90 per cent.) at 160° C.	0·60
Heavy naphthas	0·40
Crude carbolic acid	0·05
Creosote oils	46·50
Anthracene	0·74
Pitch and loss	41·21
	100·00

From another set of Simon-Carvès ovens, erected at Bear-Park, and working with a different description of coal at a somewhat higher temperature, the following results were obtained (Watson Smith, *J. Iron and Steel Inst.*) :—

	(*a*).	(*b*).	(*c*).
Ammonia water	...	...	7·44 per cent.
Light oils	5·12	5·12	6·28 „
Creosote oil	7·44	...	11·99 „
Naphthalene	...	...	10·17 „
Thick anthracene oil	34·03	...	... „
Crude anthracene	...	...	11·57 „
Naphtha	3·05	...	... „
Pitch	45·17	...	57·29 „

Further treatment gave :—

50/90 per cent. benzol	0·703	...	per cent. on tar.
Benzol, boiling, 80° to 100°	...	0·53	„ „
Toluol, „ 100° to 120°	...	0·29	„ „
Solvent naphtha, 90 per cent.	1·031	1·25	„ „
Burning naphtha, 30 per cent.	0·434	0·20	„ „
Carbolic acid (crude)	0·305	...	„ „
Cresol (crude)	0·352	...	„ „
Naphthalene (crude)	...	1·00	„ „
Anthracene, 28 per cent.	2·396	...	„ „

Specific gravity of tar = 1·15. One ton of tar yielded 1·44 gall. of 50-per-cent. benzol and 48·2 lb. of 28-per-cent. anthracene.

The Bear-Park tar is seen to resemble normal retort-tar much more closely than the Pease's West tar; it contains much more benzol and carbolic acid than the latter (although less than the lowest average of carbolic acid from gas-retort tar, viz., 0·5 per cent.). It is rather less rich in naphthalene and anthracene, but still contains a great deal of those substances.

According to private information, received from Mr S. B.

Boulton, the Simon-Carvès tar is sometimes very rich in paraffin, and this renders the anthracene made from it unsaleable, so that they have ceased making anthracene at their Bilbao works (*vide supra*).

An analysis of *tar from Otto-Hilgenstock ovens* has already been given (p. 82). Lunge and Schmid (*Chem. Ind.*, 1887, p. 337) have examined such tar—1st, from the "Germania" coke-ovens, built on the Hoffmann-Otto principle, exactly as described in the text; 2nd, from the modified coke-ovens, built according to the Ger. P. 37280 (*cf.* p. 69), at the "Hibernia und Shamrock" pit, near Bochum (Westphalia). Analysis yielded the following results:—

	A. "Germania" tar.	B. "Hibernia" tar.
Spec. grav. at 15°	1·1198	1·1368
Light oil up to 170°	6·55 p. c. weight = 7·43 p. c. vol.	4·88 p. c. weight = 5·24 p. c. vol.
Middle oil up to 230°	10·54 p. c. weight = 10·16 p. c. vol.	14·14 p. c. weight = 13·97 p. c. vol.
Creosote oil up to 270°	7·62 p. c. weight = 7·23 p. c. vol.	9·99 p. c. weight = 9·77 p. c. vol.
Anthracene oil	44·35 p. c. weight	22·65 p. c. weight
Pitch	30·55 „	43·41 „
Water	trace	3·84 „
Loss	0·39 „	1·09 „
	100·00	100·00

	"Germania" tar.	"Hibernia" tar.
Light Oil:—		
Loss by chemical washing	18·42 p. c. vol.	33·05 p. c. vol.
(including phenols)	(3·80 „)	(5·32 „)
Distillate between 78° and 100°	8·11 „	24·39 „
„ „ 100° and 140°	17·56 „	
Spec. grav. of joint distillate at 15°	0·869 „	0·862 „
Residue beyond 140°	55·91 „	42·56 „
Middle Oil:—		
Phenols (crude)	26·0 „	37·66 „
Naphthalene (crude)	43·30 p. c. weight	7·76 p. c. weight
Creosote Oil:—		
Phenols	11·0 p. c. vol.	18·33 p. c. vol.
Naphthalene (crude)	43·6 p. c. weight	4·43 p. c. weight
Anthracene Oil yielded crude anthracene, percentage on tar	4·13	0·93
Containing pure anthracene	12·90	25·67
Pitch:—		
Softening-point	165°	160°
Containing fixed carbon	51·56 p. c.	42·44 p. c.

The *distillate from the washed light oil* up to 140° could be nitrated without leaving any residue, and produced 133 per cent. weight of nitro-compounds of specific gravity 1·191, yielding only 1·1 per cent. up to 190°. It can therefore be regarded as consisting entirely of "aniline-benzol," in which a large quantity of xylene is certainly comprised. The portion boiling above 140° contained a considerable amount of naphthalene; but as this would be compensated by some naphtha, returned in the working of the middle oil, the whole of that portion may be called "heavy naphtha," without conducing to the expectation that all of it can be obtained in the state of commercial "solvent naphtha."

On rectifying the washed light oil from the "Hibernia" tar, the thermometer rose rapidly above 100°, then slowly to 140°. A considerable portion distils only above 170°. In the nitrification test 129·6 per cent. weight of nitro-compounds, specific gravity 1·188, was obtained. On distilling these compounds there escaped, between 110° and 190°, 2·47 per cent. of an oil which resisted further nitrification. Hence this "aniline-benzol" is not so pure as that from the Germania tar, and it, moreover, evidently contains very little benzene, but chiefly toluene and xylene. Its value is therefore much less than that of the benzol from the Germania tar. From the above results we can now deduce the following table of the products to be recovered from these two tars:—

	A. "Germania" tar.		B. "Hibernia" tar.	
Aniline-benzol	...	1·68	...	1·12
Heavy naphtha	...	3·64	...	2·06
Crude naphthalene from middle oil	4·54	...	1·09	
" " " creosote oil	3·15	...	0·44	
" " " total	...	7·69	...	1·53
Crude phenols from light oil	0·25	...	0·28	
" " " middle oil	1·56	...	4·90	
" " " creosote oil	0·42	...	1·75	
" " " total	...	2·23	...	6·93
Anthracene, calculated as commercial 33 per cent.	...	1·59	...	0·72
Creosote oil = middle oil + creosote, minus phenols and naphthalene	...	8·24	...	15·67
Anthracene oil filtered	...	42·76	...	21·93
Pitch (very hard)	...	30·55	...	43·41
Water	...	...	...	3·84
		98·38		97·21

An analysis of the tar obtained in beehive-ovens modified on the system described in the above-mentioned Ger. P. No. 37280 was also made at the laboratory of the Bochum mining-school, and yielded the following results :—

Spec. grav. at 19°, 1·106.
1 kg. yielded up to 160°:—20 c.c. water.
47 c.c. light oil.
1 kg. yielded up to 240°:—188 c.c. middle oil.

The light oil contained 5 per cent. acid oils, and yielded at :—

	95°-100°	110°	120°	130°	140°	150°	160°	170°	180°	190°
per cent.	2	4	12	24	38	51	64	74	80	87

The middle oil contained 24 per cent. acid oils, but very little naphthalene, and yielded at :—

	182°-190°	200°	210°	220°	230°	240°
per cent.	5	18	42	62	76	85

There was only 2·63 per cent. fixed carbon, against about 10 per cent. in other coke-tars, and about 20 per cent. in gas-tar.

Remy (*Z. angew. Chem.*, 1890, p. 327) obtained from such tar on the large scale 0·43 per cent. anthracene, 1·75 "aniline-benzol," 1·50 per cent. solvent naphtha, 34·00 creosote oil, 42·60 per cent. pitch, 8·10 per cent. water, 11·62 per cent. loss.

The tar from the Semet-Solvay coke-ovens at Glassport, Pa. (*cf.* p. 97), has the specific gravity 1·170, and yields :—

	Per cent.	
Light oil, boiling-point 80° to 170° . .	3·7	
Middle oil, „ 170° „ 230° . .	9·8	
Creosote oil, „ 230° „ 270° . .	12·0	
Anthracene oil, „ over 270° . .	4·3	71·3
Pitch	67·0	
Water	2·3	
Loss	0·9	

Complaints are still sometimes made that coke-oven tar is of unequal quality, and on the average less rich in benzol than gas-tar. But this depends upon the quality of gas-tar taken for a standard. It must not be overlooked that coke-oven tar is always obtained from the same kind of coal, unmixed with shale, boghead, or other additions frequently made at the gas-works. There is absolutely no reason why tar from the same kind of

coal, obtained in a coke-oven, should be of less uniform quality than gas-tar.

Composition of Westphalian coke-oven tar, as abstracted from Haarmann, pp. 15 and 16.

	"Germania" pit.	"Pluto" pit.
Benzol for aniline . .	1·68	0·10 to 0·30
Naphtha . . .	3·64	0·30 „ 0·90
Crude naphthalene .	7·69	5·20 „ 9·30
Crude phenols . .	2·23	0·97 „ 1·41
Creosote oil . . .	8·24	8·50 „ 11·30
Anthracene oil . .	42·76	22·00 „ 30·40
Anthracene . . .	1·59	0·71 „ 1·00
Pitch	30·55	43·20 „ 48·30
Water	...	1·20 „ 4·10

The *yield* of coke-oven tar from Westphalian coals is from 1·31 to 4·0 per cent., average 2·26. Saar coal yields about 4 per cent., Silesian coal even more. (With this we should compare the yields of tar in gas-works; Ruhr coal 4·7 per cent., Saar coal 6·1 per cent., Silesian coal 5·1 per cent.)

Schniewindt (*Min. Ind.*, 1902, 152) gives the following comparison, illustrating the difference between coke-oven tar and gas-tar in working them up by distillation :—

Fractions.	Coke-oven tar.		Gas-tar.		
	Dominion coal.	Westphalian coal.	German.	American. Good.	American. Bad.
	Per cent.	Per cent.			
Light oil . .	1·26	6·55	2·5	1·65	6·14
Middle oil .	14·73	10·54	2·5	10·66	5·03
Heavy oil .	7·07	7·62	25·0	8·18	7·50
Anthracene oil .	21·38	44·35	10·0	14·05	11·71
Pitch . .	53·03	30·55	60·0	61·16	68·25
Water . .	1·52	trace	...	1·81	...
Loss . .	1·01	0·39	...	2·48	1·37
	100·00	100·00	100·00	99·99	100·00
Free carbon .	8·10	...	25	...	48·4
Spec. gravity .	1·088	1·1198	1·155	...	1·255

A great number of similar statements on the products from various tars is made by Mallmann in *J. Gasbeleucht.*, 1905, 826.

As an outcome of all we know on the subject, we may draw the following inferences :—Closed coke-oven of the modified

Coppée type (Hoffmann-Otto's system), yield a description of tar at least equal in value to ordinary gas-tar. The "benzol" contains a large proportion of real benzene, and is practically free from non-nitrifiable products. There is a good deal of heavy naphtha. The quantities of phenol, naphthalene, and anthracene are normal. Unlike gas-tar, the tar from these ovens contains much less creosote oil and hard pitch than anthracene oil, which is rather an advantage than otherwise. All this is easily understood, since these ovens work at least at the same heat as gas-retorts.

Ovens of the beehive class, modified by applying to them *external* heating-flues and recuperators, which work at a lower temperature than those just mentioned, yield a somewhat inferior tar. The "benzol" contains very little benzene and a notable proportion of non-nitrifiable products. There is also less naphtha and much less anthracene. Moreover, it is very difficult to dehydrate. The very small proportion of naphthalene and the large proportion of phenols it contains is very noteworthy. Still this tar must be classed with gas-tar and worked up in the same way; it is entirely distinct from other tars, obtained from internally heated beehive coke-ovens of the Jameson type (p. 66).

The suggestion has been made (as mentioned in Mr Weldon's presidential address, *J. Soc. Chem. Ind.*, 1883, p. 8) that alkali-makers and other manufacturers whose establishments are situated in coal-districts, instead of feeding their furnaces with coal in the usual manner, should become coke-producers—the coke-oven gas, along with the coke, to be their fuel, whilst the tar (or oil) and ammonia were to pay for the small coal or "duff" to be employed. Thus they would get their fuel virtually for nothing. Splendid as this conception is, a calm consideration of the facts at once shows that it is impracticable, most certainly with the Jameson process, which Weldon had in view. Whether it is more practicable, when so employed, to convert all the coal at once into "producer-gas," with recovery of the by-products, we shall see later on. I. Levinstein (*eod. loco*, p. 217) believes that the suggestion mentioned by Weldon would be practicable for any manufacturer consuming at least 300 tons of coal per week, and subjecting the gas to the action of a fatty absorbent in order to recover the

benzol. Levinstein holds that the coke and the gas will be practically equivalent in heating-power to the coal carbonized; but this evidently cannot be the case, since the tar is taken out and all the heat imparted to the gases in the coke-oven must be lost in cooling the gases for the recovery of the by-products. Scheurer-Kestner (*Comptes rend.*, vol. xcvii., p. 179) calculates the loss of calorific power in transforming coal into coke and gas at 19·3 per cent., and holds Weldon's proposal to be quite impracticable.

Recovery of Ethylene from Coke-oven Gases.

Fritzsche (*J. Soc. Chem. Ind.*, 1898, 27) has proposed to recover from coke-oven gases, before burning them, not merely the benzol hydrocarbons, but also *ethylene*, by means of scrubbing them with strong (96 per cent.) sulphuric acid (after removing the benzene hydrocarbons, H_2S and moisture) in the shape of ethyl-sulphuric acid. When heating this, *ethylic alcohol* is set free, which contains no essential proportion of propylic or isopropylic alcohol or of other impurities. In this manner 26 g. absolute alcohol was recovered from 1 cbm. of coke-oven gas, but this requires a very large apparatus, as he concludes from his laboratory experiments, viz., 12·5 cbm. per 1 cbm. gas produced per minute, when employing a pressure of 4 atmospheres; nor could the difficulties be lessened by working at an essentially higher pressure. Klar (*Z. angew. Chem.*, 1899, 588) judges very favourably of this proposal, which would yield many million gallons of alcohol, and this, as he thinks, at a comparatively low figure; but it does not appear that Fritzsche's process has ever been tried on a working scale, perhaps just because it was *not* protected by a patent.

The Recovery of Benzol from Coke-oven Gases has been already described on pp. 43 *et seq.*, as it is quite similar to the processes employed for ordinary coal-gas.

Illuminating-gas from Coke-ovens.

Recently, important utterances have been made in favour of giving up the gas-retort system altogether in favour of coke-ovens of the most improved type, recovering all the by-products and yielding gas which can be enriched to any suitable extent

by the benzol recovered from the same coal, or else used as it is in lamps provided with incandescent mantles. This question has been discussed at length in a paper by F. C. Moon (*The Gas World*, 15th September 1906, pp. 512 *et seq.*), giving an account of a discussion before the Institution of Gas Engineers, raised by Thomas Glover, of which we shall now give a short abstract. The former prejudice in favour of beehive coke for metallurgical operations has at length been vanquished, and it is recognised that coke of the best quality can be produced in conjunction with the recovery of by-products; that the quantity of coke per ton of coal is higher; and that the value of the by-products is considerably in excess of the increased cost for wages, repairs, and interest charges. At present the residual gas from by-product coke-ovens is usually deprived of part of its luminosity by taking out the liquid hydrocarbons, but it is quite unnecessary to do so, and the surplus of gas left after heating the ovens is rarely made use of. On the other hand, the time seems to have come when the matter should be started from the other end; that is, the gas-works producing metallurgical coke and by-products, and using the rich gas for illumination and the poor gas for heating the ovens, etc. The Simon-Carvès Company estimates the capital cost for this purpose at £120 per ton of coal, including everything from the coal brought to the ovens to the outturn of the coke, tar, sulphate of ammonia, and benzol. For a smaller installation at a gas-works it is safe to allow £150 per ton coal carbonized per diem, and another £20 for purifying and measuring the gas, and for duplicate hydraulic mains and valves for separating the rich and poor gas. This £170 has to be compared to the corresponding items in ordinary gas-works = £300. The difference in favour of coke-ovens is £130 per diem = 13s. per ton per annum of 200 days. Allowing interest at the rate of 5 per cent., the interest charges for coke-oven plant would be 7s. 8d. per ton of coal carbonized less than for coal-gas manufacture. The products would be: 10,500 cub. ft. of gas, of which 4000 cub. ft. is available for sale, of an illuminating power certainly not below 16 candles; 8 gall. of tar, rather inferior in quality to that from gas-works; 25 lb. sulphate of ammonia and 1½ gall. of benzol, extracted from the gas used for heating the ovens.

The working costs (assuming them over 33 per cent. in excess of what is stated by a competent authority) are 1s. 8d. per ton of coke. Repairs and depreciation, allowing 7½ per cent. on the total cost, on the basis of 200 working days, gives 1s. 3d. per ton of coal carbonized, which compares with 2s. 3d. for coal-gas plant. If operating wages are taken at 1s. 8d. per ton of coke, equivalent with 1s. 2d. per ton of coal, the total charges for wages, repairs, and depreciation amount to 2s. 5d. per ton of coal carbonized.

On this basis the following comparison is made between the results of existing gas-works and those to be anticipated from the installation of coke-ovens. Two such tables are given, one for the Newcastle-on-Tyne gas-works, the other for the South Metropolitan gas-works, on published data, taking the price of metallurgical coke at 16s. 8d. at Newcastle, and 20s. in London.

NEWCASTLE-ON-TYNE, 1905.

Cost per ton of Coal carbonized at Gas-works:—

	s.	d.		s.	d.
Coal	8	6·21	Coke, *less* labour	4	4·98
Wages	2	5·40	Tar	0	9·47
Purifying	0	8·20	Ammonium Sulphate	1	6·75
Maintenance	2	0·61	10,080 cub. ft. of gas at 8d. per 1000	7	3·42
Salaries	0	4·20			
	14	0·62		14	0·62

At Coke-oven plant:—

	s.	d.		s.	d.
Coal	8	6·21	Gas, 4000 cub. ft. at 8d.	2	8·00
Purifying 400 cub. ft.	0	3·00	Tar, 8 gall. at 1d.	0	8·00
Salaries	0	4·20	Ammonium Sulphate, 25 lb. at £12, *less* cost of materials	2	1·00
Wages, incl. purifying, etc.	1	2·00	Benzol, 1½ gall. at 9d.	1	1·50
Repairs and depreciation	1	3·00	Coke, 14 cwt. at 10d.	11	8·00
	11	6·41		18	2·50
				11	6·41
				6	8·09
Credit, *less* interest charges				0	7·80
Additional profit per ton of coal carbonized				7	3·89

SOUTH METROPOLITAN GAS COMPANY.

	s.	d.		s.	d.
Coal . . .	11	0·12	Coke, *less* labour .	5	3·85
Wages . . .	2	0·58	Tar	1	2·38
Purifying . . .	0	8·67	Ammonia . . .	2	0·79
Maintenance . .	3	4·19	10,733 cub. ft. of gas at 10¼d. per 1000 ft.	8	11·33
Salaries . . .	0	4·79			
	17	6·35		17	6·35

Coke-oven plant:—

	s.	d.		s.	d.
Coal . . .	11	0·12	Gas, 4000 ft. at 10¼d.	3	5·00
Purifying 4000 ft. .	0	3·10	Tar, 8 gall. at 1d. .	0	8·00
Salaries . . .	0	4·79	Ammonia . . .	2	1·00
Wages (as above) .	1	2·00	Benzol	1	1·50
Repairs and depreciation . . .	1	3·00	Coke, 14 cwt. at 1s. .	14	0·00
	14	1·01		21	3·50
				14	1·01
				7	2·49
Credit, *less* interest charges				0	7·80
Additional profit per ton of coal carbonized .				7	10·29

On discussing the question whether it would be profitable to reserve for sale the whole of the oven gas, and employing producer gas for raising the necessary heat, it is shown in the paper, on the hand of figures, that no financial gain can be expected beyond that shown by ovens of the type in ordinary use, but a middle course might be adopted, about which we must refer to the original, as no experience exists for guidance up to the present.

Not all the recent public utterances are in favour of substituting coke-ovens for the gas-retorts. Thus Bary (*J. Gas Lighting*, 1907, 962) estimates the surplus gas available from good coke-ovens at only one-third of the whole. Schlicht (*ibid.*, p. 974), considers the question, which pays better—a gas-works of the old type, or a system of coke-ovens of the most recent type—as not yet decided.

Statistics on the Recovery of Tar and Ammonia from Coke-ovens.

We shall in the first instance quote the figures given by Haarmann (pp. 7 *et seq.*), on the *total production of coke*, some of them rounded off to entire millions. He states the productions for the years 1900 to 1902 as follows:—

	1900.	1901.	1902.
	Tons.	Tons.	Tons.
Germany	14,952,947	13,839,357	14,004,398
Great Britain	10,000,000	9,500,000	10,000,000
Belgium	2,434,678	1,885,000	2,048,070
Russia	2,250,000	1,993,000	2,000,000
France	2,289,102	1,850,000	1,850,000
Austria-Hungary	1,238,000	1,332,000	1,300,000
Spain	350,370	455,586	404,503
Sweden	9,005	60,000	60,000
Denmark	16,500	16,500	18,800
Italy	26,000	26,000	28,000
Total for Europe	33,566,602	30,957,443	31,713,771
Japan	30,000	85,680	70,000
Australia	126,213	128,882	126,872
United States	17,701,713	19,696,206	23,039,367
Canada	157,134	379,600	342,392
Total for the world	51,581,662	51,247,811	55,292,402

We now come to the *coke-ovens built on the recovery plan.* In Germany up to 1890 most ovens were still built on the open plan. Between 1891 and 1895 already 30 per cent. of the newly erected ovens were on the recovery plan, between 1896 and 1900 62 per cent., from 1901 to 1903 upwards of 75 per cent., and since 1904 no open ovens whatever have been built. In 1904 there were in Germany altogether 19,309 coke-ovens, of which 9110, or 47·2 per cent., were on the recovery plan, but these produce much more coke than the open ovens; in that year about 9,750,000 tons of coke (=57·4 per cent.) were made in the recovery ovens, against 7,280,000 tons (=42·6 per cent.) in open ovens.

In 1904 the quantity of tar produced in German coke-works was 276,805 tons, that of the gas-works only about 225,000 tons —that is, considerably less. The importation of tar from foreign

countries was 40,641 tons, the exportation from Germany, 32,872 tons. The importation also comprised considerable quantities of tar-products, viz., light oils, heavy oils, carbolic acid, naphthalene (12,444 tons), anthracene (1230 tons), and pitch, mostly from Great Britain.

The quantity of ammonia turned out by the German coke-ovens, calculated as sulphate, amounted to :—

71,118	tons in	1902
80,979	„	1903
100,212	„	1904

(More about this in Chapter XIV.)

In the West of Germany in 1904, a number of coal companies combined to erect a tar distillery for treating their coke-oven tar, under the style of: Gesellschaft für Teerverwertung, at Meiderich, near Ruhrort. This enormous factory was begun in May 1905, and started work in February 1906. Already, in 1906, 96,000 tons tar was distilled; in 1907, 129,400 tons; in 1908, 160,000 tons will be treated. Apart from the tar, considerable quantities of light oils (crude benzol) were treated, as they are recovered from the coking-gas by washing with heavy oils (pp. 43, 47); in 1907, 10,000 tons of commercial benzol were got from this source. Of pure naphthalene, solidifying at 79°·6 C., 5000 tons was made, also a large quantity of 40-per-cent. anthracene. The distillation takes place in intermittently working stills like those shown in Chapter V. The yields are, from 100 tar: 58 pitch, 30 heavy oils of specific gravity above 1·0, 0·7 crude benzol, 5 pure naphthalene, 0·55 pure 40-per-cent. anthracene, 0·05 pyridines for denaturing alcohol, 0·4 phenols calculated as pure phenol. The percentage of water in the tar worked averaged 4 per cent. (communicated to the author by the manager, Dr Spilker).

The yield of tar per cent. of the coal must needs be smaller in by-product coke-ovens than in gas-works, since the latter work a more strongly bituminous coal. Westphalian coking coal yields from 1·3 to 4, average 2·26 per cent.; Saar coal 3·9 to 4 per cent., Silesian coal still more.

Haarmann (*J. Gasbeleucht.*, 1906, 753) describes in detail the industry of by-products from coal, more especially in Germany. The development of this can be best seen from

the figures showing the number of coke-ovens built by the firm of C. Otto & Co., of Dahlhausen, which is quite at the head of this line. They erected :—

	Ovens without recovery of by-products.	With recovery of by-products.
In 1881 to 1885 . .	2144	350
„ 1885 „ 1890 . .	1886	845
„ 1891 „ 1895 . .	1371	913
„ 1896 „ 1900 . .	1206	1981
„ 1900 „ 1903 . .	638	1940
„ 1904 „ 1905 . .	none	1809
	7245	7838

We can see how the by-product ovens gradually came to the front, until in the last period they have become the only type adopted by the industry for new erections.

At the end of 1904, 47·2 per cent. of the coke-ovens in Germany were on the by-product recovery system. Since the output of these is about 50 per cent. higher than that of the open ovens, we may take it that of the 17 million tons of coke produced in Germany in 1904, $9\frac{3}{4}$ millions, = 57·4 per cent., were made in recovery ovens, and $7\frac{1}{4}$ millions, = 42·6 per cent., in open ovens.

The recovery of benzol from coke-oven gases began in Germany about 1890, and already in 1895 the yearly production was from 4500 to 5000 tons. In 1903, Kraemer (*J. Soc. Chem. Ind.*, 1903, 303) already declared that by far the greater part of the benzol hydrocarbons now found in the trade did not come from gas-tar, but from the coke-oven gases by washing them with high-boiling tar oils. The limited absorbing capacity of the market has naturally kept back the recovery of benzol from coke-oven gas, which, therefore, would not go on at the same pace as the development of the recovery ovens. The yield of benzol from the gases of Westphalian coal is from 0·3 to 0·7 per cent., from Saar coal 0·9 to 1 per cent. of the coal.

In Westphalia (Dortmund district) the production of tar during the years 1903 to 1907 increased from 132,775 tons to 381,975 tons; that of commercial benzol from 2831 tons to 15,232, of toluol from 129 to 505 tons, of xylols from 271 tons to 1631 tons, and of solvent naphtha from 164 tons to 1613 tons; that of ammonium sulphate from 53,636 tons to 155,191 tons.

The total quantity of benzol made in Germany is estimated by Haarman (*J. Gasbeleucht.*, 1906, 753) for 1904 at 36,000 to 38,000 tons. Of this the coke-ovens of the Dortmund district furnished 17,045 tons. If all the German works fitted with recovery ovens were also to recover the benzol from the gases, the yield in 1906 would be 70,000 tons—a quantity evidently much in excess of the demand.

The following figures on the coke industry in the United Kingdom are taken from *J. Soc. Chem. Ind.*, 1907, p. 1230.

		1905.	1906.
Production of blast-furnace and gas-works coke . . . . . tons		18,037,985	19,296,256
Coking coal consumed . . . . „		33,452,943	35,402,677
Number of coke-ovens in operation . .	Beehive . .	25,514	23,454
„ „	Coppée . .	2,233	2,308
„ „	Simon-Carvès .	726	808
„ „	Otto-Hilgenstock	503	768
„ „	Semet-Solvay .	470	670
„ „	Koppers . .	72	108
„ „	Simplex . .	78	78
„ „	Bauer . . .	52	52
„ „	Other types .	1,412	1,482

Returns made by 257 coking plants show that 51 of these recovered their by-products.

The number of new by-product ovens in course of construction in 1906 was: 320 Semet-Solvay, 15 Otto-Hilgenstock.

In Belgium in 1905, according to Haarmann, as much as 80 per cent. of the coke was made in by-product ovens; in France much less, in Great Britain (in 1903), 10 p.c., in the United States, 7·5 per cent.

In the United States in 1901, the total quantity of coke produced was 21,495,883 tons, of which only 1,179,900 tons were made in 1165 by-product ovens (*Iron Age*, 24th July 1902).

In 1905 there were in the United States 2380 by-product ovens on the Otto-Hoffmann system, and 1255 on the Semet-Solvay system (*Min. Ind.*, xiv., 350). The production in the United States of coal-tar was, from gas-works 41,726,970 gall., from coke-ovens 25,771,115 gall. (Atwati, in *J. Amer. Chem. Soc.*, 28, 1240).

The by-product coke-ovens in the United States produced in 1905, 26,223,323 gall. of coal-tar, 14,083 tons sulphate of

ammonia, 4,294,468 gall. ammoniacal liquor, and 4463 millions cub. ft. of surplus gas.

The following figures are given in the *United States Geological Survey* for 1907, pp. 773 *et seq.*:—

	1905.	1906.
Total production of coke in the U.S., short tons	32,231,129	36,401,217
Of these, were produced in by-product ovens . . . . . „	3,462,348	4,588,127

Number of by-product ovens working. .	1901.	1902.	1903.	1904.	1905.	1906.
	1165	1663	2061	3015	3159	3603
Do. in construction	1533	1346	1335	822	417	112

Beehive ovens in operation in 1903: 75,232, building . .	4940
New beehive ovens completed in 1906	5893
„ „ in course of construction, 1906 . .	4407

Of the 3603 recovery coke-ovens existing in 1906, 1295 were of the Semet-Solvay type, 1890 Otto-Hoffmann, 362 Rothbery, 56 Newton-Chambers (these were not working). In course of construction: 112 Otto-Hoffmann ovens, none of the other types. In 1907, 1000 retort ovens were to be built at Gary, Ind., in connection with new steel-works.

General Remarks.

Even at the present moment the greater part of the coke in the world was made without recovery of by-products. For a long time the iron makers considered the by-product coke as less valuable for their purposes than that from open ovens, but this prejudice seems to have ceased now, at least in Germany.

The general spreading of the by-product coke-ovens is, of course, kept back by the considerably higher expense of the plant, and the much greater requirements to be made of the supervision and the skill of the men, in comparison with the open ovens, in some cases also by the difficulty of disposing of the by-products at remunerative prices. This makes it intelligible, that even in Germany quite recently new coke-works have been erected on the old, open plan, since there seemed to be no chance of deriving a sufficient revenue for the much higher capital required for a recovery plant.

C. *Tar (and Ammonia) from Gas-producers.*

Since it had been proved that the process of coking coal can be performed to advantage in connection with the recovery of tar and ammonia, it was a very natural idea to extend this recovery to the gas from "gas-producers" or "generators." Attempts to solve this problem have been made in various quarters, but we shall here mention only the processes of Sutherland and Mond.

Sutherland (B. P. 3891, 1883) adds to the coal a substance capable of evolving hydrogen, and at the same time giving out an acid. He prefers for this purpose a solution of calcium chloride. Superheated steam is also employed, by combining two gas-producers with a continuous superheater and a steam-supply, the heated gas from one of the producers doing the superheating work; the hot steam, passing through the second producer, causes therein an action between the carbon of the fuel and the steam, whereby "water-gas" is produced. The gases are passed through suitable apparatus for separating the tar and ammoniacal products. The details of the producer and superheating apparatus cannot be given here.

An examination of the tar from Sutherland's gas-producers has been made by Watson Smith (*J. Soc. Chem. Ind.*, 1884, pp. 9 and 64). Its specific gravity is 1·08; it is more like ordinary gas-retort tar than Jameson coke-oven or blast-furnace tar, but it has a different smell. By distillation there was obtained from it:—

Below 230°	5·44	per cent.	by vol.	oil of sp. gr.	0·956
From 230° to 300°	10·10	„	„	„	0·996
From 300° till oils solidified	14·48	„	„	„	0·990
Oils solidifying on cooling	10·40	„	„	„	0·996
Coke	30·50	per cent.	by weight.		
Loss and water	32·60	„	„		

On redistilling the first three fractions there was obtained:—

Below 160°	0·16	per cent.	by vol.	on tar of oil.
A. 160° to 210°	0·90	„	„	„
B. 210° to 220°	2·04	„	„	„
C. 220° to 230°	15·50	„	„	„
300° till oils began to solidify	6·96	„	„	„
Soft paraffin scale	2·76	„	„	„

The oils A B C were light yellow, but darkened on standing. There was some phenol present, but no carbolic acid could be separated out. Naphthalene and anthracene were absent; of benzene but little, if any, was present. Of paraffin 6·7 per cent. on the tar could be separated.

The Sutherland-producer tar is thus seen to be entirely different from gas-tar, and is very similar to the Jameson-oven tar, but more impure than this. It is so thick that it can hardly be employed directly for creosoting without redistilling.

Several patents have been obtained by L. Mond for separating tar and ammonia from producer-gas, but as the principal stress is here evidently laid on the recovery of the ammonia, and the quality of the tar is not likely to be essentially different from that of the Sutherland-producer tar (a low temperature being expressly insisted upon), we shall treat of that process only in Chap. XII.

It should be noted that, apart from the patents actually taken out, attempts have been made in various quarters to recover by-products from producer-gases, but none of them with any financial success. The examination of a producer-tar (not derived from Sutherland's producers, but from another source), according to a private communication made to me, has shown that it contained a comparatively large quantity of anthracene, but unfortunately at the same time so much paraffin that it would be impossible on a manufacturing scale to oxidize the anthracene to anthraquinone; while, on the other hand, the paraffin obstinately retained some anthracene in spite of all purifying processes—the two substances thus mutually destroying their value.

As far as *tar* is concerned (not to speak of *ammonia* in this connection), it is clear that it would be entirely hopeless to seek for it in the producer-gases obtained from coke, anthracite, or very little bituminous coal. But precisely these are otherwise the best material for making producer-gas; bituminous coal causes difficulties in gas-producers just on account of the tar stopping up the outlets, pipes, etc. In any case it is doubtful whether it will ever pay to construct the producers in a suitable manner, and to provide them with cooling and washing plant, and to undergo the loss of heat in these operations, merely to get some tar from bituminous coal. With ammonia the

problem is different, as proved by the success of the Mond gas-producer, of which we shall treat in the part of this book devoted to ammonia.

D. *Tar (and Ammonia) from Blast-furnace Gases.*

The great majority of blast-furnaces are fed with coke, and it is evident that we cannot expect to recover either tar or ammonia from the waste gases of such furnaces. But it is otherwise with those furnaces that are fed with raw coal, in which the upper part of the furnace may be said to constitute a coking-chamber. Such an instance occurs in the West of Scotland, where there are vast beds of coal known as "splint-coal."[1] This coal is admirably adapted for direct use in blast-furnaces, since certain varieties of it agglomerate very little during coking and do not decrepitate. Scotch splint-coals contain on the average 40 per cent. of volatile matter, of which 28 to 35 go to form tar, gas, etc., and they yield on the average 50 to 55 per cent. of fixed carbon. Were the average amount of nitrogen they contain (1·35 per cent.) all evolved as ammonia, this would correspond to 142½ lb. of pure sulphate per ton (6·36 per cent.); but in blast-furnace practice only from 17 to 20 per cent. of the nitrogen of the coal is converted into ammonia. As early as 1845 Bunsen and Playfair recommended the recovery of such ammonia from blast-furnace gases, and calculated that the Alfreton furnace would yield 9½ kg. per ton. W. Jones makes the following calculation for the Scotch blast-furnaces:—Each ton of coal may be said to yield, on an average, 16 per cent. of its nitrogen as ammonia, that is, equal to 22·8 lb. of ammonium sulphate, and from 120 to 220 lb. of tar, partly in the form of vapour at the temperature of the escaping gases, partly in the state of suspension. These substances, along with a very considerable amount of dust (which must be got rid of before tar and ammonia are condensed), are contained in a volume of gas corresponding to 125,000 cub. ft. at 15°·5; but as the actual temperature varies from 204° to 343°, the gas will at, say, 260° C. occupy over 230,000 cub. ft., increased by 300 to 400 lb. of water per ton of coal in the form

[1] W. Jones, *Proc. Iron and Steel Inst.*, 1885, *J. Soc. Chem. Ind.*, 1885, p. 737, where analyses of such coal are given.

of vapour. This is thirteen times the volume of gas per ton of coal compared with that obtained in the manufacture of illuminating-gas in ordinary fireclay retorts.

From this enormous volume of gas issuing out of the blast-furnace throat, the tar and ammonia are to be condensed. For this purpose it is best, according to experience, to maintain an outward pressure on the gas. A suction or inward pressure may not only lead to disastrous explosions, but it very much reduces the yield of ammonia, owing to the entrance of air and the consequent combustion of the ammonia. The tar in the gas is scrubbed out with great difficulty, on account of its peculiar physical condition and its state of suspension in such a large volume of gas. No amount of cooling and washing is so effective as some form of violent mechanical action, such as dashing with water or otherwise.

If the whole of the gases of the furnaces at present in blast in Scotland were to be treated for the recovery of ammonia, the turn-out of ammonium sulphate would in 1885 have been some 18,000 tons per annum, equal to 22 per cent. of the production of Great Britain at that time.

The different methods for recovering volatile products from blast-furnaces may be grouped as follows :—

(I.) Methods depending on the condensation or cooling of the gas.

(*a*) Alexander and M'Cosh process, as practised at the Gartsherrie iron-works.
(*b*) Dempster process (B. P. 11250, 1884).
(*c*) Henderson process.

(II.) Methods depending upon the use of acids, without the cooling of the gas.

(*a*) Neilson's process, or Summerlee method (B. P. 440, 1882).
(*b*) Addie's process, or Langloan method (B. P. 4758, 1882).
(*c*) Chapman's process (B. P. 6406, 1884).
(*d*) Main and Galbraith's process (B. P. 10448, 1884).

Most of these processes principally, or even exclusively, tend to the recovery of the ammonia only, and will therefore be mentioned in Chap. XII.; in this place we shall describe the

principal process by which tar or oil can also be obtained from blast-furnaces.

The *Gartsherrie method* (Alexander and M'Cosh's patents,

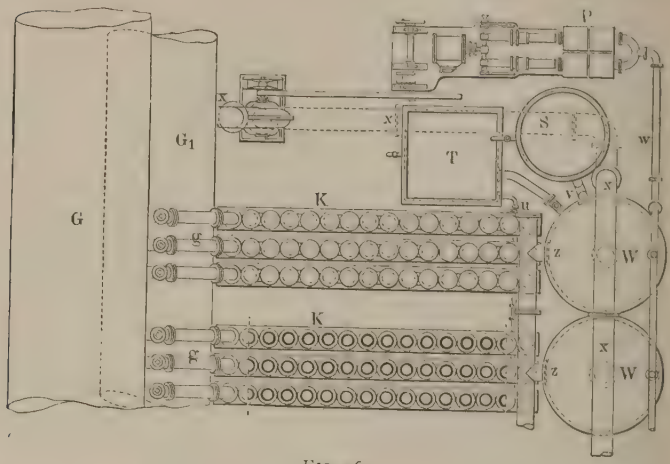


FIG. 26.

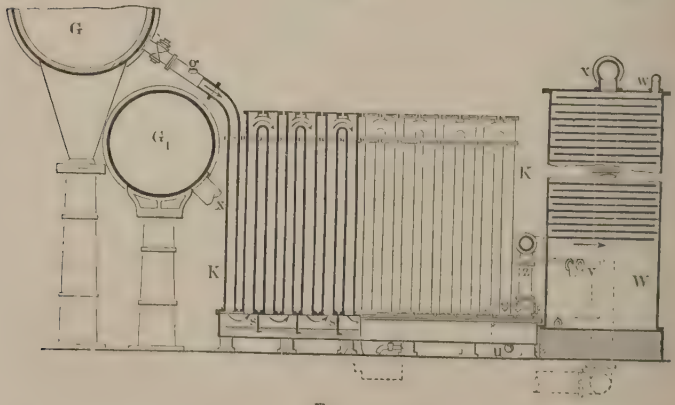


FIG. 27.

B. P. 4117, of 1879; 1433, of 1880; 3785, of 1881) is illustrated by Figs. 26 and 27. The gases pass from the furnace by the main pipe G, through pipes *g*, the number of which is in proportion to the temperature and amount of the gases, into the

coolers K, consisting of series of upright tubes, connected with each other alternately above and below, so that the gases take the course indicated by the arrows. Cooling takes place by reason of the large surface exposed by the pipes to the air. The pipe which connects the lower ends of these tubes also serves to collect condensed liquids, tar, and ammonia water; these are not permitted to rise to such a height as to obstruct the passage of the gas, but are drawn off by the overflow-pipe *u* to the tank T. The whole, as we see, is practically a copy of the ordinary air-condenser employed at gas-works. The gases pass through *z* into the washing-towers or scrubbers W, provided with perforated shelves of wood or metal, leaving alternately an open passage on one side or the other of the scrubber. A stream of water trickles from *w* down these shelves; the tar and ammonia, which have escaped condensation in K, are here condensed partly by the action of the water spread over a large surface, and partly by the continuous impact against the shelves, and pass down from W into T and S. The aqueous liquid which collects in S is pumped by P to the top of the towers, and used repeatedly, until sufficiently enriched with ammonia. The cooled and washed gases proceed by *x* to the second main G_1, to be utilized as required. If it be desired simply to eliminate flue-dust, the towers are unnecessary; but it is advisable in such a case to moisten the gases before they enter the coolers. A special apparatus for this purpose has been described by Belani.[1] I. Alexander has also constructed cooling and washing chambers of very great efficiency,[2] offering an extremely large area of water-cooled and air-cooled surface.

New patents for this purpose have been taken out by Mackay (No. 14060, 1889), the Coltness Iron Co. (No. 17673, 1889), and Imray (No. 10589, 1891).

The utilization of blast-furnace gases in Scotland is described in detail in the *Transactions of the Institution of Engineers and Shipbuilders in Scotland* for 1896, part 25, from which the following notes are taken:—A plant for treating the gases from four blast-furnaces has to deal with upwards of 35 millions of cub. ft. per 24 hours. The collecting-pipe is 7 ft. 6 in. wide, and is connected with several exhausters. The pipes are lined with

[1] *Dingl. polyt. J.*, vol. cliv., p. 257; *J. Soc. Chem. Ind.*, 1885, p. 218.
[2] *Ibid.*

fire-bricks, and first lead to a tar-washer, a square box with a sloping bottom, divided by partitions into several chambers. The partitions are nicked out at the bottom, where they dip into the tar and compel the gases to find their way through this in a multitude of small streams. This promotes an intimate contact between the tar and the gas, the complete separation of the particles of tar suspended in the gas, and, in consequence of the high temperature, the dehydration of the tar.

The gases leave this apparatus at a temperature of about 55° C., and enter the "condenser," consisting of eight sets of eighteen pipes each, 50 ft. high and 18 in. wide. The gases are made to circulate up and down, and leave the last pipes with a temperature of 22°. During hot weather the upper parts of the pipes are cooled by sprinkling water upon them. The tar and ammonia condensed here are separated by lying undisturbed in a "separator." The gases now pass another "washer," 60 ft. long, 12 ft. wide, and 7 ft. high, fed with ammoniacal liquor, which is here made sufficiently strong for working up into sulphate of ammonia, and the tar condensed is used in the "tar-water" previously mentioned. Behind this are fixed the three exhausters, each with a capacity of nearly a million cub. ft. of gas per hour and provided with pressure-gauges. The gas, after passing the exhausters, is lastly forced through another washer, fed with water and intended to retain the remaining ammonia and tar; the liquors condensed here are used for feeding the preceding washers. The purified gas then passes to the steam-boilers and the heating-stoves for the blast, where it is burned.

The tar is distilled in stills uniformly heated with purified gas; the ammonia-water is distilled in column-apparatus by means of steam, and the ammonia converted into sulphate.

From each ton of coal fed into the blast-furnaces is obtained 7 gall. of tar-oil, 86 lb. of tar-pitch, and 25 lb. of sulphate of ammonia. The purified gas suffices for raising all the steam required for the blowing-engines, for working part of the regenerative blast-heating stoves, for distilling all the tar, and for evaporating part of the washings from the ammonia-stills.

At a Meeting of the Iron and Steel Institute, held 5th and

6th May 1898, Riley reported that on an average from 1 ton of coal 130,000 cub. ft. of gas is obtained; the by-products represent 20 per cent. of the price of the coal. The gas (as confirmed by Mond) is perfectly well adapted for gas-motors, which are in constant use up to 250 h.p., with a saving of 45 per cent. as compared with the coal burnt under steam-boilers. The cost of plant is considerable, but it is quickly repaid by the profits.

In 1891 there were 77 blast-furnaces in Scotland (*Alkali Reports*, 1891, p. 13), working with coal suitable for the recovery of tar and ammonia, 57 of which were provided with recovery-plant. Whilst a blast-furnace of average size, including the blowing-engines, costs £7800, the condensing-plant alone costs more than that; the 57 plants in question have cost £444,600. In England only 3 blast-furnaces are provided with recovery-plant, at a cost of £12,000 per oven.

The following process described in the *Zeitschr. f. Berg-, Hütten- und Salinenwesen*, 1895, p. 172, as being employed at an English iron-works, presents some interest. Beside the blast-furnaces there is a kiln, 15 ft. high, charged with 50-per-cent. pyrites, which is kept burning by a blast of air. The mixture of air and sulphurous-acid gas thus formed is introduced into the pipe carrying away the blast-furnace gas, and here sulphate of ammonia is formed. The hot gases are now passed through a tower filled with shelves over which water is constantly run. The liquor here formed is pumped up again until it is sufficiently strong, and ultimately the solution of sulphate of ammonia is separated from the tar by settling.

A paper by R. Hamilton in the *Journal of the West of Scotland Iron and Steel Institute*, No. 4, January 1902 (*Stahl. u. Eisen*, 1902, p. 509), reports on the present state of the recovery of by-products from the Scotch blast-furnaces. We give a brief *resumé* of this very interesting paper (which necessarily treats of ammonia as well as of tar). During the twenty years since the introduction of this new industry, more progress has been made in erecting new plants and extending those formerly built than in further improvements of the process. The Gartsherrie process of Alexander and M'Cosh (p. 132), which is working since 1881, has proved the simplest means, viz., cooling the gases and washing with water, suffice for a complete

recovery of the by-products. At first the tar, whose quality is entirely different from that of gas-tar, was almost unsaleable; later on, certainly, uses have been found for it as well. This led to the invention of Addie's "Langloan" process (p. 181), which aimed at producing merely ammoniacal compounds, by bringing the gas into contact with SO_2 (from burning pyritic shale). This process worked from 1884 till 1892, but the difficulties were too great, and it was definitely abandoned in favour of the Dempster process (p. 181).

A similar process was tried but given up again, at the Summerlee Iron Works. The gases were not cooled, but at once brought into contact with sulphuric acid. Main and Galbraith's process, which works with hydrochloric acid, as well as a process invented by Hamilton himself, where ammonium carbonate is produced, have no interest with respect of the recovery of *tar*. Hamilton then quotes a number of experiments, bearing on the influence of the *water* contained in the ore. This, of course, would influence the yield of ammonia much more than that of the tar, but it is felt even with respect of the latter. English ores containing much water produced much less ammonia from the same coal than the Scotch ores, containing less water. But by roasting the English ore *no* improvement in the yield of tar and ammonia was effected; the cause of this behaviour of the English ore has not yet been cleared up. When the coal was distilled by itself, it yielded 214 lb. tar per ton. When mixed with English ore in the same proportion as in the blast-furnace, the yield of tar fell to 66 lb., and of the NH_3 44 per cent. was lost. Scotch ore acted in a similar way. If in lieu of ore, sand was mixed with the coal, 170 lb. of tar was obtained, which proves that the loss of tar and NH_3 is not attributable to the mere presence of foreign solid matter.

The total quantity of tar recovered from the gases of the Scotch blast-furnaces in 1900 is estimated by Hamilton = 122,000 tons (along with 16,559 tons sulphate of ammonia).

Composition of Blast-furnace Tar.

The tar recovered from blast-furnaces has been repeatedly examined by Watson Smith (*J. Soc. Chem. Ind.*, 1883, p. 495;

J. Chem. Soc., 1886, vol. xlix., p. 17). Its specific gravity was found = 0·954. Distillation yielded:—

		Per cent. by volume.	Per cent. by weight.	Sp. gr.
Below 230°	Water	30·60	32·3	1·007
	Oil	2·91	2·8	0·899
230° to 300°		6·97	7·1	0·971
300° until oils solidify		13·02	13·5	0·994
Oils solidifying on cooling (soft paraffin scale)		16·75	17·3	0·987
Coke		...	21·5	...
Loss		...	5·5	...

The oils were quite transparent, the lower-boiling and lighter fractions possessing an amber-yellow colour, the higher-boiling ones having a colour approaching that of port wine. On standing a day or two they all considerably deepened in colour, especially the heavier fractions, which possessed a strong green fluorescence.

A further examination of the distillates proved that naphthalene is present in very small quantity; anthracene could not be detected, but small quantities of toluene, xylene, and pseudocumene were isolated. The xylene proved to consist principally of the meta-isomer (priv. comm. from Watson Smith). About 0·54 per cent. of hard paraffin was obtained from the tar, and a considerable amount of phenols, among them true carbolic acid. By successive treatment with caustic soda and sulphuric acid, the distillates answering to the carbolic oil and creosote oil of ordinary coal-tar yielded 23·1 per cent. by volume of phenols, and 11·09 per cent. by volume of basic substances.

This large proportion of phenols, far exceeding what can be obtained in a similar manner from ordinary gas-retort coal-tars, seems to some extent to confirm the theory of K. E. Schulze (*Annalen*, vol. ccxxvii., p. 143), according to which at least a considerable proportion of the aromatic coal-tar hydrocarbons is formed by the breaking-up, at higher temperatures, of first-formed phenols into the elements of water and hydrocarbons. Since blast-furnace tar, both on account of its being formed in the top part of the furnaces and also because of its chemical and physical properties, is evidently a low-temperature product

as compared with the tar obtained from gas-retorts and close coke-ovens (Carvès', Otto's, etc.), it might *à priori* be supposed that it was an intermediary mixture, and to contain, so to speak, the half-way phenol constituents in predominating quantity. On the contrary, it contains but a small quantity of the lowest phenol (carbolic acid), $C_6H_5 . OH$, and cresols, $C_6H_4(CH_3) . OH$, much less than gas-retort tar, which would seem to show that Schulze's theory can hardly extend to the formation of benzene itself. The decomposition of the higher-boiling phenols of blast-furnace tars by means of hot zinc-dust or hot iron-borings yielded a large quantity of xylenes, and proved the original presence of metaxylenol, $C_6H_3(CH_3)_2 . OH$, in accordance with Schulze's theory; the still higher-boiling fractions, treated in the same way, indicated the presence of pseudocumenol, $C_6H_2(CH_3)_3 . OH$, and of naphthols, $C_{10}H_7 . OH$. Of course other phenols and phenol-ethers might also be present.

In any case, blast-furnace tar is altogether different from ordinary gas-retort tar, and cannot be employed for the same purposes. It would require to be redistilled, and would then yield creosoting-oils of good quality and lubricating-oils of indifferent quality.

Uses of Blast-furnace Tar.—Allen and Angus (B. P. 11689 of 1887) distil blast-furnace tar, extract those constituents of the distillate which are soluble in alkali, and precipitate the solution by means of carbon dioxide, in the shape of furnace-gases. By repeated solution and fractional precipitation, as well as by fractional distillation, the products are separated. The volatile products are used as disinfectants, the heavy products for pickling timber. The hydrocarbons are worked up for paraffin-oil, lubricating-oil, and gas-oil. (This patent contains nothing which had not been previously known.)

Blast-furnace creosote oil is now largely used for pickling timber, for the "lucigen-light," and as fuel. The phenols contained therein (25 to 35 per cent. against 5 to 10 per cent. in heavy gas-tar creosote oil) resemble those from wood-tar, lignite, or shale-oil; they are sold as an antiseptic, under the name of "neosot," and are said to be equal in antiseptic powers to "liquid carbolic acid," but with much less corrosive properties

(*Chem. Trade J.*, 1887, p. 122). This is confirmed by a new investigation by Watson Smith (*J. Soc. Chem. Ind.*, 1887, p. 583). The tar from the Gartsherrie blast-furnaces is rather lighter than water; it contains much paraffins, but anthracene could not be discovered, perhaps owing to the presence of the paraffins. The quantity of phenols is very large; besides phenol proper we find metacreosol, metaxylenol, pseudocumenol, and naphthols. The hydrocarbons found were: toluene, xylene, (over 70 per cent. metaxylene), pseudocumene, mesitylene, and a little naphthalene; benzene was never found in such tar, but is perhaps present in the gases. The basic constituents resemble those of coal-tar; aniline was found among them.

E. *Tar obtained in the Manufacture of Water-gas.*

This manufacture, which is especially flourishing in the United States, is now also carried on to a considerable extent in Europe; consequently "water-gas tar" is also coming into the market, especially in America.

Water-gas is, as is well known, obtained by the action of superheated steam on white-hot coke or anthracite. It consists essentially of hydrogen and carbon monoxide, and can be employed directly for heating purposes, but for lighting purposes it must be "carburetted" by means of volatile hydrocarbons. This is usually done by passing the gas, together with the vaporised hydrocarbons, through red-hot retorts. In this process, if the superheater be not too hot, about 25 per cent. of the oil is recovered as tar, which is frequently run to waste (Douglas, *J. Gas Lighting*, 1891, p. 1130).

This tar contains about 50 per cent. water, with which it forms an emulsion not separable by the usual means. Douglas has succeeded in separating the oil from the water by heating the tar in closed boilers at a pressure of 10 atmospheres. He thus obtained from 100 parts of crude tar, 50 parts dehydrated tar with only 1 per cent. moisture, and 25 parts water, the remainder of the water evaporating during the process. According to Douglas, this dehydrated tar is readily saleable, but he does not say what is done with it.

A. H. Elliott (*Amer. Chem. J.*, 1884, p. 248) obtained the following results with water-gas tar:—

Specific gravity, 1·100.

400 c.c. on fractional distillation yielded volume per cent.:—

Fraction I., 80° to 200° . . .	9·2	$\frac{1}{3}$ oil. $\frac{2}{3}$ water.
„ II., 200° „ 270° . . .	11·2	solids.
	17·7	oil.
„ III., 270° to the formation of pitch . . .	6·0	solids.
	26·5	oil.
„ IV.	1·7	semi-solid mass.
	6·0	oil.
	78·3	per cent.

The solid portion of fraction II. consisted principally of naphthalene, and contained only 0·82 per cent. anthracene = 0·09 per cent. of the weight of tar. From fraction III. 2·33 per cent. anthracene of the weight of tar could be obtained. The solid portion was a greenish-yellow mass, containing 25·6 per cent. anthracene; the oils contained only 3 per cent. anthracene. Fraction IV. still yielded about 2 per cent. anthracene, almost equally divided between the semi-solid portion and the oil, Thus the total percentage of anthracene would amount to 2·63 per cent. of the tar—that is, from six to ten times as much as in coal-tar.

Nevertheless this tar seems to possess but little value. According to a communication from Mr S. B. Boulton, water-gas tar, which is now frequently mixed with London gas-tar, contains so much paraffins that the preparation of anthracene from such a mixture is unremunerative, and buyers therefore object to getting water-gas tar with coal-gas tar. It is also mixed with so much water (50 to 75 per cent.), that it forms an emulsion which is difficult to separate even on prolonged standing. But Vivian B. Lewes states (*J. Gasbeleucht.*, 1902, p. 329) that the introduction of water-gas into coal-gas retorts has an influence merely on the quantity, not on the quality of the tar.

Matthews and Goulden (*Gas World*, xvi., p. 625) found in water-gas carburetted with Russian crude oil:—

	Per cent.
Benzene	1·19
Toluene	3·83
Light paraffins	8·51
Solvent naphtha	17·96
Phenols	trace
Middle oils	29·14
Creosote oil	24·26
Naphthalene	1·28
Anthracene (crude)	0·93
Coke	9·80
	96·90

The percentage of anthracene in this case is also very high.

Scholvien, in a German patent of 1904 (No. 163623), states that the water-gas tar, obtained in the treatment of petroleum hydrocarbons for the purpose of preparing carburetting agents, cannot be distilled on account of its large percentage of water, and had hitherto merely been utilized for making pitch or as fuel. Even when mechanically dehydrated, it can be distilled only on a small scale. He treats it, therefore, by a special process (Ger. P. 161236), of which we shall speak in Chapter V.

F. *Tars and Tar-products obtained by Superheating certain Oils and Vapours.*

The decomposition of compounds belonging essentially to the "fatty" ("aliphatic") series, by passing their vapours through red-hot tubes, and the fact that aromatic compounds are formed in this way, has been studied by Berthelot (since 1867) and several other chemists. The preparation of illuminating gas, which always contains considerable quantities of aromatic compounds, from oil and other fatty substances, has been practised according to this method for a long time. This process, the "*oil-gas process*," seems to have been invented by John Taylor, in 1814,[1] and was introduced into Germany in 1828, but soon mostly abandoned, since the oil was found to be too expensive. It was taken up again after 1850, when cheap mineral oils, from shale and lignite, came into the market; and in America the refining of petroleum yielded a large quantity of oil suitable for the above purpose. The oil-gas industry

[1] Scheithauer, *Die Fabrikation der Mineralole*, etc., 1895, p. 282.

was principally developed in Germany by H. Hirzel, Hübner, and others, but chiefly by Julius Pintsch, whose compressed oil-gas has been widely employed for lighting railway carriages, both in England and Germany.

We cannot in this place enter into the details of the manufacture of oil-gas, and only mention that the raw material, the so-called gas-oil, has generally a specific gravity of 0·850 to 0·900, and has to pass over up to 320° C. According to Hirzel, 100 kl. gas-oil should yield 60 cbm. gas of an illuminating power of 7·5 German standard candles, with an hourly consumption of 35 litres.

In that manufacture the oil, introduced into a red-hot retort, is first volatilized and the vapours are decomposed into more volatile bodies in contact with the hot walls of the retort. Part of the oil escapes decomposition and is condensed in a receiver; another portion is converted into aromatic hydrocarbons, with secretion of carbon, the former being also condensed in the receiver. Thus *oil-gas tar* is formed. According to Young (*J. Gas Lighting*, 1893, ii., p. 260), many paraffins are formed by the radiant heat within the retort, and mostly aromatic hydrocarbons by contact of the vapours with the hot sides of the retort; this should be taken into account when constructing apparatus, either with the view of producing an illuminating gas or of obtaining benzol, etc.

The following table gives some idea of the percentage composition of oil-gas as compared with coal-gas:—

	Oil-gas.	Coal-gas.
Carbon dioxide	1·0	1·5
Oxygen	0·5	1·4
Heavy hydrocarbons	33·0	3·0
Carbon monoxide	2·5	8·0
Hydrogen	15·0	48·7
Methane	46·0	33·7
Nitrogen	2·0	4·0

On compressing oil-gas to 10 or 12 atmospheres, each 100 cbm. of compressed gas separate about 6 to 10 kl. liquid hydrocarbons. This liquid has been examined by Armstrong (*vide supra*, p. 39) and by Bunte (*J. Gasbeleucht.*, 1893, p. 442), who found in it:—26 per cent. benzene; 15 per

cent. toluene; 5 per cent. higher aromatic hydrocarbons; 10 per cent. olefins.

The oil-gas tar proper, of which 30 to 45 per cent. of the oil employed is obtained, is even now considered a troublesome by-product. In colour and smell it resembles coal-tar; but its specific gravity is 0·950 to 1·000, and it is much thinner. Its exact composition has not yet been ascertained, but it must vary very much, according to the raw material used, the temperature of its generation, and the shape of apparatus. Scheithauer quotes the following boiling-points:—

Between 70° and 150° C. . .	5 to 10 per cent.
„ 150° „ 200° „ . .	5 „ 10 „
„ 200° „ 250° „ . .	20 „
„ 250° „ 300° „ . .	20 „
Above 300°	30 „
Residue and loss . . .	10 „

The investigations of Scheithauer (*loc. cit.*), Pryce (*J. Gasbeleucht.*, 1893, p. 497), Macadam (*J. Gas Lighting*, 1893, p. 400), Lewes (*ibid.*, p. 699), and Armstrong (*vide supra*, p. 39), proved the presence of very small quantities of benzene, and rather more toluene and its homologues, but principally olefins and acetylenes, sometimes also low-boiling paraffins; also 3 to 4 per cent. naphthalene. Some oil-tars are entirely free from anthracene, others contain 0·06 up to 1 per cent. This anthracene contains considerable quantities of methyl-anthracene. Free carbon occurs in large quantities, but phenols and basic bodies are excluded by the nature of the raw material.

Oil-gas tar is sometimes worked up by distillation. This process yields a light naphtha employed for carburetting gas, a middle fraction sold as "solvent naphtha," and a heavy fraction which is either employed for making new gas or as "boring-oil" in the iron industry. The residue forms a thick tar, much used instead of natural asphalt. Much of the oil-gas tar is burned at the gas-works, either mixed with other fuel or else by itself, by means of the "forsunka." Zimmer & Gottstein (Ger. P. 98071) work it up with Portland cement for the purpose of obtaining an extremely resisting material.

The principal use of that description of tar seems to be in the following direction. Although the discovery of benzene itself, by Faraday, was made in the liquid condensing from

compressed oil-gas, it is only quite recently that the *preparation of substances similar to coal-tar*—that is, containing considerable quantities of benzene, naphthalene, and anthracene—*from the heaviest distillates and residues of the petroleum and paraffin-oil refineries*, by superheating them in red-hot tubes, has been attempted on a practical scale. Special experiments to ascertain how far this reaction might be applicable on a practical scale were made in response to a prize offered in 1877 by the Berlin Society for the Promotion of Industry. It was required to be shown that it is possible to convert the high-boiling oils of the browncoal-tar, by a technically applicable process, into the hydrocarbons forming the basis of the aniline-colour and alizarin industry.

Liebermann and Burg[1] found that the above oils, when passed through red-hot tubes filled with porous material, are converted into a mixture of hydrocarbons very similar to coal-tar, containing about 4 per cent. benzene and toluene and 0·9 per cent. crude anthracene. Petroleum and vulcan oil yielded much gas and benzene, but hardly any anthracene. Coal-tar oils, boiling between 140° and 150° and between 150° and 210°, when treated in a similar way, suffered much less loss of weight. The quantitative results obtained by those chemists are, from their own showing, no guide as to those obtainable on the large scale, for which special experiments would be required. Similar to the above were the results of Salzmann and Wichelhaus[2]; and Atterberg[3] proved the same for wood-tar.

The most extended paper on this subject has been published by Letny.[4] He examined a tarry condensate, produced in the manufacture of gas by passing heavy petroleum "tailings" through red-hot tubes filled with wood; after several passages through the retort he found it entirely similar to coal-tar, and especially proved it to contain benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene, along with unchanged petroleum. After this he tried passing the petroleum-tailings on a small scale through a ret-hot tube filled with charcoal. He obtained 33·3 per cent. of gas and 66·6 per cent. of tar, containing much amylene, benzene, toluene, xylene, and higher-boiling oils, but no solid hydrocarbons. The absence of the latter was

[1] *Ber.*, 1878, p. 723. [2] *Ibid.*, pp. 802, 1431. [3] *Ibid.*, p. 1222.
[4] *Dingl. polyt. J.*, ccxxix., p. 353.

ascribed by Letny to the comparatively small thickness of the layer of red-hot charcoal which the petroleum-vapours had to pass on the small scale. At a higher pressure more oils of low boiling-point were formed, but on the whole less tar and bad gas.

The raw material for Letny's experiments was the residue from refining the petroleum of Baku in South Russia (*cf.* Chapter IV.). Since it has been shown by Beilstein and Kurbatoff that this petroleum contains principally hydrogen addition-products of the benzene series, isomeric, but not identical, with the fatty compounds of the series C_nH_{2n}, it is easily explained how large quantities of benzenoid hydrocarbons could be obtained by the igneous decomposition of that substance.

More recently the tar obtained in superheating naphtha residues has been examined by Dziewonski (*Chem. Rev.*, 1902, p. 36; *Chem. Zeit.*, 1902, p. 492).

In 1879, experiments made at my laboratory on a somewhat large scale by a chemist sent there by one of the largest Russian petroleum refiners (Ragosine), with an apparatus constructed by myself, fully confirmed the fact that large quantities of benzene, toluene, naphthalene, and anthracene could be obtained from petroleum residues in the above-described manner. In 1881, as reported by Rudnew,[1] in fact, the tar from the Kasan gas-works, where petroleum residues form the raw materials for gas-making, was distilled in the ordinary way; it yielded 10 to 12 per cent. of benzol, up to 5 per cent. of naphthalene, and some anthracene, but hardly any phenols.

In 1882, according to Liebermann,[2] the working-up of petroleum residues in the above-described manner was industrially carried out by the Brothers Nobel at Baku. The anthracene prepared by them tested 25 to 30 per cent., and at the Ludwigshafen works yielded very good alizarin. The naphthalene was pure. The benzol, although boiling at 80° to 85°, was unsuitable for nitrobenzol, as it contained too many fatty hydrocarbons; but it can be easily purified by freezing at −14° (a process easily practicable in Russia during winter), even when containing 30 per cent. of impurities, and thus made to yield pure nitrobenzene, boiling at 205°. The naphtha residues are dropped into red-hot iron retorts filled with pumice; they yield,

[1] *Dingl. polyt. J.*, ccxxxix., p. 72.
[2] *Ibid.*, cclvi., p. 429; *J. Soc. Chem. Ind.*, 1883, p. 128.

per 1000 kg., 500 cbm. (= 17,650 cub. ft.) of gas, employed for heating and lighting, together with 300 kg. of tar, containing 0·6 per cent. of crude anthracene and 17 per cent. of crude benzol (boiling at 120°, and, indeed, containing only about 4 or 5 per cent. of benzene and toluene).

In the year 1882 there were produced at Baku 200,000 tons of naphtha residues, which were sold as fuel for steamboats, etc., and for the manufacture of gas in Russia; but only a very small proportion of this was worked for benzol and anthracene. The outlay for plant is extremely large. Kraemer found that, employing pipes 5 to 6 in. wide and 7 to 9 ft. long, two set in one furnace, no more than 2 cwt. of residues could be passed through in 24 hours. By his mode of purification he was able to prepare oils containing 91 or even 96 per cent. of nitrifiable benzol; whilst Liebermann's method yielded to him only oils containing 24 per cent. of nitrifiable benzol.

Statements concerning the Russian trials of employing petroleum residues ("astatki") as sources of benzene, naphthalene, and anthracene, have been made by B. Redwood (*J. Soc. Chem. Ind.*, 1885, p. 79), from observations made during a visit to Baku in 1884. He mentions a "cupola regenerative furnace" patented by Nobel, and quotes the following details obtained from that gentleman. The first treatment gives 30 to 40 per cent. of tar, containing 15 to 17 per cent. of 50-per-cent. benzol. By a second destructive distillation of heavy oils remaining in the tar after the separation of the benzol, 70 per cent. of tar is obtained, containing from 7 to 10 per cent. of 50-per-cent. benzol, 16 per cent. of naphthalene, 2 or 3 per cent. of dry "green grease" (containing 30 per cent. anthracene), and 24 per cent. of pitch. There is also obtained in the process 75 to 100 cub. ft., per cubic foot of astatki, of gas having an illuminating-power five times greater than that of coal-gas. The regenerative furnace is first heated to 1000° C. (astatki being, of course, the heating-agent), and after having become cooled during the process of decomposing the astatki, it is again similarly heated, the gas remaining in the furnace and the coke deposited on the hearth being utilized as fuel. The furnace is stated to remain in working order without cleaning for twelve months. The process, in spite of being carried out on a somewhat large scale, had evidently not passed beyond the experimental stage, and

has no doubt been stopped since Redwood's visit, owing to a fall in prices. Engler, who visited the same district in 1885, reports nothing of it.

Another trial of the same method was made in the United States by a Swiss chemist, who had seen something of the experiments made in my Zurich laboratory (see p. 145); but although a good deal of capital was sunk in the enterprise, the result was most unsatisfactory, either owing to that chemist's inexperience or to the adverse nature of American petroleum residues, which do not seem to have the same composition as the similar material obtained in the Caucasus.

Hlawaty (*Chem. Ind.*, 1891, p. 69; Ger. P. 51553) passes strongly superheated steam into a mixture of petroleum residue, etc., with one-third sawdust and one-sixth quicklime. The vapours are passed through red-hot pipes filled with iron or carbon, and are then subjected to condensation. The liquid obtained contains much aromatic hydrocarbons; the gases consist mostly of acetylenes, and, after passing through a purifying mixture of lime, copperas, and sawdust, they are conducted through red-hot pipes filled with pumice, where they furnish another aromatic condensate. In lieu of steam, the superheated vapours from ethyl or methyl-alcohol or acetic acid may be employed.

Boissieu (*Chem. Zeit.*, 1893, p. 70) found that Russian "massud" (petroleum residue), differently from shale oil or American petroleum, furnishes 12 to 15 per cent. aromatic products by dry distillation. According to him, this quantity would be increased by employing extreme cold and compression in the condensers. The crude benzol thus obtained yielded 69 per cent. at 100°, 96 per cent. at 140°, and the total yield was 8·04 per cent. benzene, 2·57 per cent. toluene, and 1·05 per cent. xylenes. The aniline and toluidine made therefrom were of excellent quality.

Nikiforow (B. P. 19957, 1886, and 21374, 1901) splits up the residues into fractions by strong heat applied under pressure. They are first vaporized under ordinary pressure in a semi-oval cast-iron retort at 515° to 550°. The receiver is kept at 200°, so that only high-boiling products are here condensed, which are either burnt underneath the retorts, together with the permanent gases, or again subjected to decomposition. The vapours issuing from the first receiver are cooled down in a

worm, and the condensing liquid is distilled in ordinary tar-stills provided with reflux-coolers. The fractions up to 100°, 130°, 160°, 180°, and 200° are separately condensed; the residue is used like the tar from the first receiver. Each fraction is separately treated in an oil-gas retort, two of which are always combined; they are here decomposed at temperatures varying from 700° for the lightest to 1200° for the heaviest fraction, under a pressure of two atmospheres. The first receiver is kept at 150° or 200°; the vapours uncondensed here are condensed by cooling, fractionally distilled, and aniline-benzol recovered from the fraction boiling up to 120°. The fractions up to 160°, 180°, and 200° re-enter the cycle of operations; those above 200° are worked for naphthalene and anthracene. The tar collected in the first vaporization may be dealt with in a similar manner, treating the fractions at much higher temperatures under pressure, but yields much less aromatic hydrocarbons. The total yield of these is about 12 per cent. Nikiforow's process has been carried out on a large scale at Kineshma, in Russia, employing high temperature and pressure. By the first distillation of the naphtha or naphtha residues, 38 per cent. tar is obtained, half of it consisting of aromatic hydrocarbons. At the second distillation these are obtained in a sufficiently pure state, the yield being 12 per cent. benzene and toluene, 2 or 3 per cent. naphthalene, 1 per cent. anthracene. The German patent No. 143549, awarded for this process, was cancelled a few years after, and the manufacture in Russia was stopped after a fire. The cost of the benzol obtained by this process was 1·06 mark per kilogram—that is, four or five times that of English benzol. A favourable report on Nikiforow's process was made by Oglobine (*Z. angew. Chem.*, 1905, 406), but the stoppage of the factory proves that it did not pay.

Recently Nikiforow has taken out a British patent, No. 17,450 of 1907, for the following process. Hydrocarbons of a boiling-point not exceeding 200° C., obtained by the destructive distillation of naphtha, are pulverised by directing a current of water-gas, issuing from a suitable nozzle against a jet of the oil previously heated to 200° C., and the mixture is caused to pass through a retort. The water-gas is previously heated in a coil to a temperature of 800° to 1000° C., and to keep up the heat

more water-gas of the same temperature is introduced into the retort at both ends. By this means aromatic hydrocarbons are formed which collect together with soot in a catch-box provided with a stirring-arrangement, whilst the gases and uncondensed hydrocarbons escape. The condensed hydrocarbons are drawn off through an overflow, and when working at 800° to 850° C., the products are stated to be: 15 per cent. of commercial benzene, 4 per cent. of naphthalene, 0·5 per cent. of anthracene, 10 to 12 per cent. of coke, 9 per cent. of coked material and soot, and 50 per cent. of gas of 14 candles illuminating power.

Dvorkovitch (B. P. 21647, 1892; *J. Gas Lighting*, 1893, ii., p. 1083) has constructed an apparatus on the lines laid down by Young (p. 142), which has been erected at Ragosine's works at Nischni-Nowgorod, and is stated to yield 40 kl. 50-per-cent. benzol from 100 kl. petroleum. One hundred kilolitres of Russian petroleum yield 46·7 cbm. gas of 60·3 standard candles, with an hourly consumption of 150 litres, and 37 per cent. tar. The latter yields: 32·4 per cent. benzol, 41·1 per cent. light oil, 0·14 per cent. anthracene, 11 per cent. pitch, and 11 per cent. lubricating-oil.

Wisse and Schneller (B. P. 21343, 1892) propose employing an electrically heated furnace for the decomposition of these residues. Seigle (*J. Gas Lighting*, 1893, ii., p. 629) employs a lead bath. Another furnace for a similar purpose has been constructed by Meffert (Ger. P. 99254).

All these proposals have at the present day hardly more than scientific interest. On the one hand, it is now known that these residues can be converted into valuable lubricating-oils and asphalt; on the other hand, there is no lack of products from coal-tar, and no necessity to produce similar substances in such a roundabout way. For the same reason the proposals of Dvorkovitch, referring to the manufacture of gas, in which the loss of gas and illuminating-power is to be compensated by the value of benzol, etc. (p. 32), have been adversely criticised by Scheithauer (*loc. cit.*) and Lewes (*J. Gas Lighting*, 1893, ii., p. 619).

G. *Synthetic Production of Aromatic Hydrocarbons by means of Barium Carbide.*

Bradley and Jacobs (Ger. P. 125936) heat barium carbide with barium or sodium hydrate at 600° to 1200° C., whereby

benzol, naphthalene, and anthracene are formed according to the equation (for benzene):

$$3BaC_2 + 3Ba(OH)_2 = C_6H_6 + 6BaO.$$

The yield is stated to be very good, but at the present low prices of those products there is hardly any chance for this process.

General Observations on Coal-tar from various Sources.

All the above-mentioned varieties of coal-tar, to which we might add natural tars—as the Rangoon naphtha and, in a wider sense, even crude petroleum—are principally (although never exclusively) composed of hydrocarbons; but these belong to very different classes, and the members of these classes are present in various proportions. In some of them the "aromatic" hydrocarbons—that is, those belonging to the benzene series in its widest sense—are altogether predominant; and these "*benzenoid*" tars are those which yield the raw material for the manufacture of coal-tar colours—benzene, toluene, xylene, naphthalene, anthracene, and carbolic acid. In other tars, which we call the "*paraffinoid*" tars, we find, apart from phenols of higher orders, the members of the paraffin series and others closely related to it, as the olefines, all of them belonging to the "aliphatic" or "fatty" compounds. Some of these tars are stated to contain compounds which, although isomeric with paraffins or olefines, are yet in reality aromatic compounds, namely, hydrogen addition-products (*cf.* next chapter); but this does not seem to make any practical difference in the way in which such tars can be utilized (that is, merely for the manufacture of burning and lubricating-oils and of solid paraffin), while they are useless for the manufacture of coal-tar colours.

As a rule, the members of both series are found to a certain extent in all kinds of tar; and this is a rule without exception, if we include the phenols, which are all "aromatic" compounds, and which do not seem to be ever absent in any coal-tar. Those tars are most valuable which contain most benzenoid hydrocarbons; even a rather small proportion of paraffinoid hydrocarbons greatly lessens their value for colour-making, and any

considerable admixture of such may make them practically worthless for that purpose. Benzol, containing many "unnitrifiable" oils, is not accepted by any aniline manufacturer; and anthracene containing paraffin is dreaded by every alizarin maker. Hence the practical value of some of the tar-producing processes described above is very questionable, since they yield a mixture of benzenoid and paraffinoid compounds containing too much of the latter kind. It is of course not impossible that good and cheap manufacturing methods will be found for separating these two kinds of compounds; but until that is the case, those processes have no chance of competing with gas-tar and with some descriptions of coke-oven tars.

It is, of course, an important question: What are the conditions under which the formation of benzenoid or that of paraffinoid compounds predominates? We have already seen (p. 17 *et seq.*) that differences of temperature have a great deal to do with it; but this does not account for everything. Without doubt the physical condition and the chemical composition of the coal distilled are of great importance: older fossils yield more benzenoid hydrocarbons, younger ones more paraffins and phenols (p. 25). But even when treating one and the same material, ordinary gas-coal or coking-coal, great differences are observed according to the method of applying the heat. We will illustrate this by the following quotation from a paper by Watson Smith (*Industries*, 1886, p. 139):—

"In the cases in which the benzenoid tars (those useful for coal-tar colours) are yielded, the condition which must be observed is an intense heat applied to a relatively thin layer of the fuel. If this condition be not observed, consecutive distillation occurs, in which, in the interior of the mass of coal (a comparatively bad conductor of heat), or in that part of the oven or retort in which the heat is less intense, products of the paraffinoid class mainly are first distilled at the lower temperature there existing, pass outwards to the exterior, and escape in such abundance into the highly heated oven or retort space, and thence are so rapidly drawn-off to the condensing arrangements that a large proportion of the paraffinoid matters still predominate in the product condensed.

"In the other case, however, in which the layer of fuel is sufficiently thin, sufficiently exposed on all sides to the intense

heat, as fast as the constituents of the coal rearrange themselves to form the products at all, they do so almost directly to form the high-temperature products and benzenoid constituents, and the consecutive is almost entirely merged in a more or less direct process.

"The truth of these observations is well illustrated in the forms, mode of heating, and general arrangement of the ordinary gas-retorts, and in the Simon-Carvès coke-ovens, and, in opposition to them, the Jameson's adapted beehive coke-ovens, where the coal lies in a dense mass spread out on the floor of the same, which is not heated below; nor are the sides heated, but the heat is applied to the upper surface of the carbonizing fuel. Also, in another form of the adapted beehive coke-oven the coal lies in a dense mass on the floor, which is heated strongly by flues passing below the floor or bed; but neither sides nor top are heated, and if the top were heated there would be too great a space between it and the fuel. In both the latter cases, paraffinoid tars are produced."

To this we need only add that the same conditions as exist in the case of gas-retorts and Simon-Carvès coke-ovens for producing benzenoid tars are offered by the Otto coke-ovens and other similar forms; while the conditions for the predominance of paraffinoid compounds are also furnished as a natural consequence of their mode of action, by gas-producers and blast-furnaces working with coal.

Determination of the Yield of Tar and Ammonia from Coal.

It is, of course, desirable to know beforehand what quantity of tar and ammonia a new description of coal may be expected to yield. Such estimations would certainly be far more important if tar and ammonia ever became the principal products of the distillation of coal; but we have seen above that this state of affairs, which at one time seemed to be approaching, is now once more relegated to a distant future. Under present circumstances the quantity and quality of the gas and the coke obtained in distillation are decidedly the primary considerations.

Nevertheless it occasionally happens that either coal-owners or coal-consumers wish to enlighten themselves as to the yield

of by-products from some special description of coal. Hitherto the only reliable means of arriving at that result has been to distil some truck-loads of coal in the same retorts or ovens which are used for the ordinary manufacture, taking care that the by-products are separately collected. This is not very easy, especially so far as the tar is concerned, since there is always a good deal remaining from previous operations in the hydraulic main, etc.; but it can be done by special care, and we have already noticed (pp. 30, 31) such experiments performed at Munich and Paris.

This test is, of course, not always possible to perform, and it is very desirable to arrive at the yield of by-products by a test on the laboratory scale. Instead, however, of describing any apparatus or process for this purpose, I will point out the difficulties of such testings. At the very least there should be provided an experimental retort, imitating the conditions on the large scale as closely as possible; for instance, a small cast-iron D-shaped retort, 18 in. long and 6 in. high (inside measurement), with a head, cover, and gas-delivery tube similar to those of ordinary gas-retorts, in which about 10 lb. of coal can be distilled. Even here the conditions are very different from those of a real gas-retort; and we must expect to get a very different quantity of tar, and of quite different quality, from that which the same coal will produce in a full-sized fireclay gas-retort or a coke-oven. In the case of ammonia, also, the small distillation is no guide as to the large one. It is, of course, utterly hopeless to expect anything like trustworthy retorts when chemists (as is the case) work with even smaller apparatus, such as glass combustion-tubing, porcelain tubes, or gun-barrels. S. Schmitz[1] believes he can obtain good results in testing for ammonia by passing the gases evolved in distilling 10 or 15 g. of coal in a combustion-tube over red-hot coke contained in the first half of the tube; but here it is uncertain how much of the ammonia is derived from the coal distilled, and how much from the action of the gases and vapours on the coke, which always contains nitrogen (Chapter XII.). The gases are absorbed in dilute sulphuric acid, the liquid evaporated to a small volume with the addition of oxide of mercury, and the ammonia driven off by caustic soda. This method will at best allow comparative

[1] *Stahl u. Eisen*, 1886, p. 396.

results to be obtained for different kinds of coal, but it cannot be expected that these results will coincide with manufacturing practice.

General Observations on the Supply of Coal-tar for Industrial Purposes.

At first, as mentioned p. 4, the tar was nothing but a disagreeable by-product in the manufacture of gas, which had to be removed at some expense. In fact, it was a nuisance which, to some extent, impeded the rapid extension of that form of illumination. During the first period of gas-making the tar was simply run to waste; but this was soon stopped by the nuisance caused in the neighbourhood of the works. The first trustworthy note on the value of gas-tar is found in Dumas's *Treatise of Applied Chemistry* (German edition, 1830, vol. i., p. 762), from which it appears that at the Paris gas-works it fetched 8s. per ton, apart from, small quantities sold for medicinal purposes at about 1d. per lb.

In England, as we shall see in Chapter V., already before that time attempts had been made to utilize coal-tar by distillation, employing the volatile portions as burning-naphtha and in the manufacture of waterproof clothing, in lieu of essence of turpentine.

But all this amounted only to a local and inefficient outlet for coal-tar: all the more as the gas-manufacture extended at a much greater rate than the above industries. A great change took place after Perkin's discovery of mauve, in 1856. The new industry of coal-tar dyes required correspondingly large quantities of raw materials, especially benzol and, later on, anthracene; and this naturally led to a great extension of the distillation of coal-tar. In this respect Great Britain just as naturally took the lead, owing to its flourishing gas-manufacture, and she has been ruling the market in respect of tar-products ever since.

Thus coal-tar had acquired considerable value; and, on the other hand, the enormously increasing manufacture of beetroot-sugar greatly stimulated the demand for sulphate of ammonia, employed as manure, and almost exclusively obtainable from the gas-liquor. About 1884, according to a report of the

Directors of the South Metropolitan Gas Company, the sale of tar and sulphate of ammonia realized the sum of 9s. 5½d. per ton of coal distilled. Since the price of coal was 11s. 9d. per ton, the value of the by-products of gas-making amounted to 82 per cent. of that of the coal employed.

From a private but trustworthy source, the author can quote the following prices obtained for tar and tar-products about that time :—

Coal-tar in 1883 at gas-works, 55s. ; at tar-works, 61s. to 63s. per ton.

Coal-tar in 1884 at gas-works, 35s. per ton.

Pitch, 33s. to 35s. per ton.

Benzol, 50 to 90 per cent., 3s. to 3s. 1d. per gall. (with cask).

Crude carbolic acid, 1s. 8d. to 1s. 9d. per gall.

Light oil (redistilled), sp. grav. 0·967, 7d. per gall.

Crude naphtha, yielding 50 per cent. at 170° C., 1s. 4d. per gall.

Fluid heavy oil, 2¼d. to 3¼d. per gall. in bulk.

Sulphate of ammonia, good grey, 24 per cent., £14, 10s. in bags (had been as much as £20 a few years previous).

According to other sources, the price of 90-per-cent. benzol in 1883 was 14s. per gall. (no doubt only during a short time).

In 1885, however, the price of coal-tar had fallen to about 12s. ; during 1886 (in England) it was about 7s. per ton, and that of 90-per-cent. benzol 1s. 8d. per gall. This decline shows no sign of abatement. In Germany coke-oven tar in May 1886 sold at 23s. per ton.

In 1887, coal-tar fetched 15s., benzol 90-per-cent. 3s. 6d. per gall., pitch 13s. 6d. per ton, anthracene 1s. per unit, sulphate of ammonia (grey) £12, 15s. per ton.

In Germany the price of coal-tar reached its maximum in 1885 : 45 marks (say £2, 4s.) ; the minimum of 17 marks (16s. 8d.) was in 1898, and for several years it has been pretty steady at 23 marks (£1, 2s. 6d.) per ton. The price of benzol has fluctuated there even more. In 1882 it attained the famine price of 400 marks (say £20) per 100 kg. In 1885 it was already down to 50 marks (£2, 10s.) ; from 1899 to 1904 it has been from 20 to 21 marks, say, roundly, £1 per 100 kg.

The cause of the great depreciation of the value of coal-tar (ammonia will be treated of in that respect later on) is not quite

clear. It is true that the great fall in the price of aniline-colours and alizarin, which took place about the same time, and which was undoubtedly owing to over-production, must have influenced the value of coal-tar. Much stress has also been laid on the fact that during those years the most strenuous efforts had been made to obtain benzol, tar and ammonia from coke-ovens, blast-furnaces, gas-producers, and so forth. But the quantity of tar, of a quality similar to that of gas-tar, which had been actually obtained in Great Britain up to this time, must have been only a small fraction of that produced at the gas-works; as we have seen before (pp. 111, 138), the blast-furnace tar and the Jameson tar cannot at all compete with gas-tar, and the producer-tar can hardly be said to be an article of commerce at the present time.

The state of affairs on the Continent was different, especially in Germany. That country is now in a position to furnish almost the whole of the requirements of coal-tar products for its colour-industry, the largest in the world. Nor has this been changed by the exertions made to develop the recovery of by-products in coke-making in Great Britain, where this system had made comparatively slow progress until the last few years.

Whilst the demand of coal-tar products in the manufacture of aniline-dyes and other colouring-matters has been steadily increasing, this has not been the case with another very promising outlet for benzol, viz., for carburetting lighting-gas. A check has been given to the latter by the development of the incandescent gas-light, and recently also by that of acetylene-light.

The depreciation of gas-tar, following from the competition of coke-tar, was also furthered by the fact that the percentage of benzol in the former has been gradually decreasing with the increasing introduction of producer-firing at the gas-works. It is also a fact that the coal consumed by the latter does not at present yield so much benzol as in former years—probably because the best quality of coal is now used up by the coke-works, as giving a higher yield of coke.

At the present time, the quantity of tar coming into the market from gas-works and coke-works seems to cover the demand, which tells upon the price (*vide supra*).

A further decline is not unlikely to take place during the

next few years, for it is a well-known fact that if the supply of a certain commodity continuously, even if but slightly, exceeds the demand, its price is depreciated far out of proportion to the amount of surplus, and the opposite takes place if the demand exceeds the supply. But whilst in most other cases the effect of this is, up to a certain extent, counteracted by the storage of large quantities, both of the raw materials and of the products of manufacture, and by fluctuations in the production of both, it is very different in our case. Gas-tar, on the one hand, must be produced quite irrespective of the demand, since it cannot be avoided in gas-making, and, on the other hand, its storage for any length of time is a practical impossibility. Hence a comparatively slight excess of the supply, which cannot be checked in the way usual with most other raw materials, generally soon causes an intolerable glut in the market, and must rapidly force down the price.

This case, however, seems to be excluded here. The recovery of by-products in coke-making requires a very costly plant, and extends only as far as the prices of tar and ammonia keep up at a certain figure. On the other hand, the gas-works are at all times in a position to get rid of any excess of tar by burning it under the retorts. Its value for this purpose greatly exceeds that of coke: in Germany it is estimated that it pays burning the tar under the retort when its price has fallen below 17s. per ton, but in England the limit must be placed very much below that figure. Another way of dealing with the tar, viz., converting it into gas, has been frequently attempted, but success in that direction is not yet secured.

The fear entertained some years ago, that the enormous development of electric lighting might greatly reduce the manufacture of gas, and consequently the supply of tar, has not been realized. Quite as much gas is produced as in former times, more especially since it is now so much used for heating and for gas-engines; nor has the introduction of water-gas (which is not incompatible with the production of tar) had as yet any influence in that direction. If the demand for tar (and ammonia) should ever increase beyond the capacity of the present producers, there is still a vast field for the production of more tar; for even in Germany there are still a great many coke-ovens working without recovery of by-products, and in

most other countries they are in a small minority against the old system, where no by-products are recovered.

If we further look at the various processes for extracting benzene, etc., from ordinary coal-gas (*vide supra*, p. 36 *et seq.*), for converting petroleum-residues and other hitherto almost valueless substances into aromatic compounds by the effect of high temperature, and other similar efforts to be mentioned later on, we shall see that there is not the slightest fear of any scarcity of those indispensable raw materials which are the subject of this treatise.

When surveying the manifold sources, not at all, or at least very imperfectly, utilized up till now, from which tar and ammonia can be obtained by means decidedly within our grasp, it would seem useless to speculate, as has been occasionally done, as to what would be the state of affairs if, by processes to be invented hereafter, all the enormous quantities of coal consumed in our households, for raising steam, and for innumerable other purposes (where a recovery of by-products is not at present thought of) should be made to yield up their tar and ammonia as well. It is easy to get out startling figures, say 5,000,000 tons of coal-tar and 1,000,000 tons of ammonium sulphate for Great Britain alone, but such figures are altogether illusory. They cannot frighten those who are interested in keeping up the price of those materials at a remunerative rate, nor can they offer a solid prospect of benefiting the consumers of those materials—that is, ultimately, the general public; for if ever practicable means should be invented for burning coal in the above-mentioned cases in such a way that the by-products could be collected (perhaps by means of gas-producers), the interest upon the frightful cost of plant and the inevitable working-expenses of collecting the tar and ammonia would probably far more than outstrip any profit that might accrue from their sale, taking into consideration the extremely low price which tar and ammonia would command after the opening out of the more accessible sources of supply from coke-ovens, etc., long before the more remote sources just spoken of could come into play.

CHAPTER III

THE PROPERTIES OF COAL-TAR AND ITS CONSTITUENTS

Coal-tar is a black, more or less viscid fluid of peculiar smell, of specific gravity 1·1 to 1·2, usually between 1·12 and 1·15; London tar averages 1·2, and sometimes amounts to 1·215; country tars are lighter; cannel-coal tars still more so.[1] It has been asserted by some that tar is more valuable the lower its specific gravity. In any case, this could only be said of pure coal-tar; but since the tar from cannel-coal, shale, etc., which contains more toluene and paraffin than coal-tar, is much lighter than the latter, the above criterion is not in any way to be depended upon.

Coal-tar is an extremely complex mixture of chemical compounds, some of which have not yet been even isolated. Thus comparatively little is known of the indifferent oils occurring in its distillation, between the phenols and naphthalene on the one hand, and anthracene oil on the other; neither do we know all the compounds existing in crude anthracene, and still less those constituting the pitch, but considerable progress has been made in this direction during recent times. Whether some of the constituents of coal-tar are already present in the coal, and are therefore simply evolved by the ordinary process of distillation, must be left an open question. It can hardly be doubted that coal contains aromatic compounds; probably it is entirely made up of such, and contains no free carbon at all. But it is another question

[1] It is strange that authors like Bolley, Wurtz, Girard and Delaire, Vincent, and others have stated the specific gravity of coal-tar to be equal to or below that of water. Evidently there has been confusion with tar from browncoal or boghead, etc.; and a wrong quotation of this kind has passed from one book to another without criticism.

whether any of these compounds are volatile, without change, at the temperature existing in the gas-retorts.

Tar contains nitrogenous compounds chiefly of a basic nature, owing to the nitrogen always found in the coal, and sulphur compounds, derived from the pyrites, etc., never absent in coal.

E. J. Mills (*J. Soc. Chem. Ind.*, 1885, p. 326) gives the following ultimate analyses of London and of average Scotch cannel gas-tar :—

	London.	Scotch cannel.
Carbon . .	77·53	85·33
Hydrogen . .	6·33	7·33
Nitrogen . .	1·03	0·85
Sulphur . .	0·61	0·43
Oxygen . .	14·50	6·06
	100·00	100·00

Since tar always contains a considerable quantity of ammoniacal liquor mechanically mixed with it, we must expect to find all the constituents of the latter in the tar ; also all those of the gas probably occur in the tar, being absorbed by it.

The following is an enumeration of the compounds hitherto found in coal-tar or reasonably presumed to exist in it ; they will subsequently be described in detail :—

	Formula.	Melting-point.	Boiling-point.
A. HYDROCARBONS.		°C.	°C.
I. *Methane Series*, C_nH_{2n+2}.			
Methane	CH_4		
Ethane	C_2H_6		
Propane	C_3H_8	...	−20
Butane (normal)	C_4H_{10}	...	+1
Pentane (normal)	C_5H_{12}	liquid	37
Isopentane	C_5H_{12}	,,	30
Hexane (normal)	C_6H_{14}	,,	69
Heptane (normal) . . .	C_7H_{16}	,,	98
Ethylisoamyl	C_7H_{16}	,,	90·3
Octane, I.	C_8H_{18}	,,	119–120
,, II.	C_8H_{18}	,,	124
Nonane, I.	C_9H_{20}	,,	130
,, II.	C_9H_{20}	,,	150·8
Decane, I.	$C_{10}H_{22}$	,,	158–161
,, II.	$C_{10}H_{22}$	,,	170–171

	Formula.	Melting-point.	Boiling-point.
A. HYDROCARBONS (*continued*)		°C.	°C.
I. *Methane Series* (continued)			
Undecane	$C_{11}H_{24}$	liquid	180-182
Duodecane	$C_{12}H_{26}$	,,	200-202
Tredecane	$C_{13}H_{28}$	,,	218-220
Quatuordecane	$C_{14}H_{30}$	,,	236-240
Quindecane	$C_{15}H_{32}$	,,	258-262
Sedecane	$C_{16}H_{34}$	,,	280
Solid Paraffins	$C_{17}H_{36}$ to $C_{27}H_{56}$	40-60	250
II. *Ethylene Series*, C_nH_{2n}.			
Ethylene	C_2H_4	...	-110
Propylene	C_3H_6	...	,,
Butylene (normal)	C_4H_8	...	-5
Pseudobutylene	C_4H_8	...	+1
Isobutylene	C_4H_8	...	-8
Amylene	C_5H_{10}	liquid	+39
Hexylene	C_6H_{12}	,,	69
Heptylene	C_7H_{14}	,,	98
III. *Hexahydro-Addition-products of the Benzene Series*, C_nH_{2n} (*Naphthenes*).			
Hexahydrobenzene	C_6H_{12}	liquid	69
Hexahydrotoluene	C_7H_{14}	,,	97
Hexahydroisoxylene	C_8H_{16}	,,	118
IV. *Acetylene Series*, C_nH_{2n-2}.			
Acetylene	C_2H_2		
Allylene	C_3H_4		
Crotonylene	C_4H_6	liquid	18
Valylene (?)	C_5H_8		
Hexoylene	C_6H_{10}	,,	80
Higher members	$C_{12}H_{20}$	,,	210
,, ,,	$C_{14}H_{24}$	,,	240
,, ,,	$C_{16}H_{28}$	,,	280
V. *Tetrahydro-Addition-products of the Benzene Series*, C_nH_{2n-2} (*Naphthylenes*).			
Tetrahydrobenzene	C_6H_{10}	liquid	83
Tetrahydrotoluene	C_7H_{12}	,,	103-105
Tetrahydroxylene	C_8H_{14}	,,	129-132
VI. *Series* C_nH_{2n-4}.			
Cyclopentadiene	C_5H_6	liquid	42·5
Nonone	C_9H_{14}	,,	174
VII. *Aromatic Dihydro-Addition-products*, C_nH_{2n-4} (*Terpenes*).			
Dihydrobenzene	C_6H_8	liquid	84
Dihydrotoluene	C_7H_{10}	,,	105-108
Dihydroxylene	C_8H_{12}	,,	132-134
Dihydrocymene	$C_{10}H_{16}$	,,	174

	Formula.	Melting-point.	Boiling-point.
A. HYDROCARBONS (*continued*)		°C.	°C.
VIII. *Benzene Series*, C_nH_{2n-6}			
Benzene	C_6H_6	+5·1	81·1
Toluene	C_7H_8	liquid	111
Xylene	C_8H_{10}	,,	
Orthoxylene	...	,,	143
Metaxylene	...	,,	139
Paraxylene	...	15	138
Pseudocumene	C_9H_{12}	liquid	168
Mesitylene	C_9H_{12}	,,	164
Hemellithol	C_9H_{12}	,,	175
Durene	$C_{10}H_{14}$	80	190
Other tetramethylbenzenes	...		
IX. *Naphthenes.*			
X. *Styrolene* (?), C_nH_{2n-8}	C_8H_8	liquid	145
Hydride of styrolene (?)	C_8H_{10}	,,	
XI. *Indene*, C_nH_{2n-10}	C_9H_8	,,	178
Methylindene	$C_{10}H_{10}$	,,	195-200
Dimethylindene	$C_{11}H_{12}$		
Hydrindene	C_9H_{10}	,,	174
XIA. *Dicyclopentadiene*	$C_{10}H_{12}$	40·5	170
XII. *Naphthalene*, C_nH_{2n-12}	$C_{10}H_8$	80	218
Naphthalene dihydride	$C_{10}H_{10}$	liquid	200-210
,, tetrahydride	$C_{10}H_{12}$	,,	204
α Methylnaphthalene	$C_{11}H_{10}$	,,	243
β Methylnaphthalene	$C_{11}H_{10}$	32·5	242
Dimethylnaphthalene	$C_{12}H_{12}$	liquid	262-264
XIII. *Acenaphthene*, C_nH_{2n-14}	$C_{12}H_{10}$	95	277·5
Acenaphthene hydride	$C_{12}H_{12}$	...	260
Diphenyl	$C_{12}H_{10}$	70·5	254
XIV. *Fluorene*, C_nH_{2n-16}	$C_{13}H_{10}$	113	295
XV. *Anthracene*, C_nH_{2n-18}	$C_{14}H_{10}$	213	360
Anthracene dihydride	$C_{14}H_{12}$	106	305
,, hexahydride	$C_{14}H_{16}$	63	290
,, perhydride	$C_{14}H_{24}$	88	250
Methylanthracene	$C_{15}H_{12}$	208-210	above 360
Isomethylanthracene	$C_{15}H_{12}$	202-204	
Dimethylanthracene (?)	$C_{16}H_{14}$	224-225	
Phenanthrene	$C_{14}H_{10}$	99	340
Phenanthrene tetrahydride	$C_{14}H_{14}$	liquid	300-304
Phenanthrene octohydride	$C_{14}H_{18}$	,,	
Phenanthrene perhydride	$C_{14}H_{24}$	−3	270 275
Pseudophenanthrene (?)	$C_{16}H_{12}$	115	above 360
Synanthrene (?)	$C_{14}H_{10}$	189-195	
Fluoranthene	$C_{15}H_{10}$	109	above 360

	Formula.	Melting-point.	Boiling-point.
A. HYDROCARBONS (*continued*)		°C.	°C.
XV. *Anthracene* (continued)			
Pyrene	$C_{16}H_{10}$	148	above 360
Chrysene	$C_{18}H_{12}$	250	436
Chrysene hydride	$C_{18}H_{28}$	liquid	360
Chrysene perhydride	$C_{18}H_{30}$	115°	353
Chrysogene	...	280-290	
Retene	$C_{18}H_{18}$	98-99°	350
Retene dodecahydride	$C_{18}H_{30}$	liquid	336
Succisterene (?)	...	160-162	above 300
Picene	$C_{22}H_{14}$	364	518-520
Picene eikosihydride	$C_{22}H_{34}$	liquid	360
Picene perhydride	$C_{22}H_{36}$	175	360
Benzerythrene	$C_{24}H_{18}$	307-308	
Crackene	$C_{24}H_{18}$	308	over 500
Bitumene	...	...	...
Truxene	$C_{27}H_{18}$	365	...
B. OXYGENIZED COMPOUNDS.			
Water	H_2O	0	100
Methylic alcohol (?)	CH_4O	liquid	63
Ethylic alcohol (?)	C_2H_6O	,,	78·5
Acetone	C_3H_6O	,,	56
Ethylmethyl ketone (?)	C_4H_8O	,,	77·5-81
Acids and Phenols.			
Acetic acid	$C_2H_4O_2$	16	119
Benzoic acid	$C_7H_6O_2$	121	249
Phenol (carbolic acid)	C_6H_6O	41	184
Orthocresol	C_7H_8O	32	187
Paracresol	,,	36	201
Metacresol	,,	3	202
Xylenols: Ortho 1, 2, 4	$C_8H_{10}O$	62	225
Meta 1, 2, 3	,,	73	216
Meta 1, 3, 4	,,	26	211·5
Para 1, 2, 4	,,	74·5	211-213
α Naphthol	$C_{10}H_8O$	96	280
β Naphthol	,,	123	294
Phenols of the Anthracene series (?)		?	
α Pyrocresol	$C_{15}H_{14}O$	196	350
β Pyrocresol	,,	124	
γ Pyrocresol	,,	105	
Rosolic acid (?)	$C_{19}H_{14}O_3$		
Brunolic acid (?)			
Cumarone	C_8H_6O	liquid	169
p-methyl-cumarone	C_9H_8O	,,	197-199
m-methyl-cumarone	,,	,,	195-196
o-methyl-cumarone	,,	,,	190-191
o,p-dimethyl-cumarone	$C_{10}H_{10}O$	,,	221-222
m,p-dimethyl-cumarone	,,	,,	221
o,m-dimethyl-cumarone	,,	,,	216
Diphenylene oxide	$C_{12}H_8O$	81-85	275·5

	Formula.	Melting-point.	Boiling-point.
C. SULPHURETTED COMPOUNDS.		°C.	°C.
Hydrogen sulphide	H_2S		
Ammonium sulphide	$(NH_4)_2S$		
„ sulphocyanide	$(NH_4)NCS$		
Sulphur dioxide	SO_2		
Carbon bisulphide	CS_2	liquid	47
„ oxysulphide	COS		
Mercaptanes			
Alliol (?)			
Thiophene	C_4H_4S	liquid	84
α Thiotolene	C_5H_6S	„	113
β Thiotolene		„	113
α-α Thioxene	C_6H_6S	„	135-136
α-β Thioxene		„	136-137
α-β^1 Thioxene		„	137-138
β-β Thioxene		„	136-137
α-β-β Trimethylthiophene	$C_7H_{10}S$	„	163
Tetramethylthiophene	$C_8H_{12}S$	„	182-184
Biophen	$C_4H_4S_2$	„	165-170
α^1-α dithienyl	$C_8H_6S_2$	33	
β^1-β dithienyl		„ 132·4	
Trithienyl	$C_{12}H_8S_3$	147	357
Thionaphthene	C_8H_6S	30-31	220-221
Thiophthene	$C_8H_4S_2$	liquid	224-226
Diphenylene sulphide	$C_{12}H_8S$	?	?
D. CHLORINATED COMPOUNDS.			
Ammonium chloride	NH_4Cl		
E. NITROGENIZED COMPOUNDS.			
I. *Basic.*			
Ammonia	NH_3		
(Ammonium compounds mentioned under C, D, & E II.)			
Methylamine, ethylamine, etc.	...	liquid	
Cespitine (?)	$C_8H_{13}N$	„	95
Aniline	C_6H_7N	−8	182
Toluidines	C_7H_9N	...	197-199
Pyridine	C_5H_5N	liquid	116·7
α Picoline	C_6H_7N	„	135
β Picoline		„	138
γ Picoline		„	(?)
αα Lutidine	C_7H_9N	„	143
αβ Lutidine		„	162-163
αγ Lutidine		„	157
$\alpha\beta_1$ Lutidine		„	(?)
βγ Lutidine		„	163·5-164·5
$\beta\beta_1$ Lutidine		„	169-170
γ Ethylpyridine		„	164-166
$\alpha\gamma\alpha^1$ Collidine	$C_8H_{11}N$	„	171-172
$\alpha^1\beta\gamma$ Collidine		„	165-168

	Formula.	Melting-point.	Boiling-point.
		°C.	°C.
E. NITROGENIZED COMPOUNDS (*con.*)			
I. *Basic* (continued)			
Parvoline (?)	$C_9H_{13}N$	liquid	188
$\alpha\beta\gamma\beta^1$ Tetramethylpyridine	„	„	232-234
Coridine (?)	$C_{10}H_{15}N$	„	211
Rubidine (?)	$C_{11}H_{17}N$	„	230
Viridine (?)	$C_{12}H_{19}N$	„	251
Leucoline (Chinoline)	C_9H_7N	„	239
Isoquinoline	C_9H_7N	28	236
Chinaldine (α Methylquinoline)	$C_{10}H_9N$	liquid	243
Iridoline (γ Methyllepidine)	$C_{10}H_9N$	„	252-257
Cryptidine (Dimethylquinoline)	$C_{11}H_{11}N$	„	274
Tetracoline-Octacoline (?)			
Acridine	$C_{13}H_9N$	107	above 360
2-Methylacridine	$C_{14}H_{11}N$	134	
4-Methylacridine	„	88	
2-4-Dimethylacridine	$C_{15}H_{13}N$	71	
Hydroacridine	$C_{13}H_{11}N$	107	
II. *Not Basic.*			
Pyrrol	C_4H_5N	liquid	133
Ammonium cyanide	$CN.NH_4$		
Methylic cyanide (acetonitrile)	$CH_3.CN$	„	79
Benzonitrile	C_6H_5CN	„	196
Methylic isocyanide	C_2H_3N	„	59·6
Carbazol	$C_{12}H_9N$	238	355
Phenyl- α naphthyl-carbazol	$C_{16}H_{11}N$	225	above 440
Phenyl- β naphthyl-carbazol	„	230	
F. FREE CARBON	C_x		

HYDROCARBONS OF THE METHANE SERIES, C_nH_{2n+2}.

These hydrocarbons are sometimes called hydrides of monad radicals—also paraffins, because a mixture of the higher solid members of the series, as obtained in the distillation of shale, etc., had obtained that name from its great resistance to chemical reactions (*parum affinis*). This mixture, however, contains also non-saturated hydrocarbons (olefins).

The compounds of this series are principally formed in the destructive distillation of wood, peat, shale, browncoal, boghead, cannel-coal, etc., and from coal also when distilled at a comparatively low temperature. Most descriptions of natural petroleum consist of a mixture of all the members of this series. In coal-tar they play a subordinate part; but if, in gas-making, coal has been partly replaced by browncoal, shale,

cannel-coal, etc., the tar is much richer in aliphatic hydrocarbons, and may easily contain so much of them that the extraction of the aromatic hydrocarbons does not pay—especially as the aliphatic hydrocarbons are most objectionable impurities in commercial benzol, which, if they occur to any great extent, may render it unfit for the manufacture of nitrobenzol.

The compounds of this class are distinguished from the non-saturated hydrocarbons (the ethylene and acetylene series) by not being absorbed by sulphuric acid or bromine; this behaviour can be utilized for separating the two classes. From benzene and its homologues they are distinguished through being hardly at all acted upon by nitric acid in the cold, and not forming nitro-compounds.

The lowest members, up to butane, are at the ordinary temperature gaseous, but may occur in tar in a state of solution, all the more readily as they are easily soluble in ether and alcohol, and thus probably also in benzene, etc. The members from pentane upwards are liquid; up to decane they have been observed in tar. The highest members, beginning from $C_{18}H_{38}$, are solid, and form paraffin proper: whether this occurs in tar obtained exclusively from ordinary coal is doubtful.

Methane, CH_4.

Synonyms—methylic hydride, marsh-gas, fire-damp, light carburetted hydrogen. A colourless gas, devoid of smell or taste; sp. gr. 0·5566 (air = 1). At 0° C. 100 vols. of water absorb 5·45 vols.; alcohol nearly half its volume. It burns with a pale yellow flame. Passed through red-hot tubes it yields acetylene, benzene, naphthalene. Mixed with air it gives a very explosive mixture.

Ethane, C_2H_6.

Syn. dimethyl, ethylic hydride. A gas without colour or smell; sp. gr. 1·075; condenses at 4° to a liquid under a pressure of 46 atmospheres. Water dissolves at 0° 9·45 per cent. by volume, alcohol 1½ times its volume. Burns with a bluish, non-luminous flame.

Propane, C_3H_8.

Syn. propylic hydride. A gas, condensing to a liquid below $-20°$ C.; alcohol dissolves six times its volume.

Butane, C_4H_{10}.

Syn. diethyl, butylic hydride. Two isomers are possible and known; only normal butane, however, $CH_3—CH_2—CH_2—CH_3$, has been found in mineral oils. Sp. gr. 2·01 (air = 1). Authorities differ widely as to its boiling-point. Frankland puts it at $-23°$; Butlerow at $+1°$, and, under pressure of $2\frac{1}{4}$ atmospheres, at $+18°$. In water it is next to insoluble. Alcohol at 14° C. and 745 mm. pressure dissolves 18·13 vols. It burns with a strongly luminous flame.

Pentane, C_5H_{12}.

Syn. amylic hydride. Of the three isomers the normal and isopentane, $CH_3—CH_2—CH(CH_3)_2$, have been found in cannel- and boghead-tar. Schorlemmer found in coal-tar only normal pentane.

Normal pentane boils at from 37° to 39° C., sp. gr. at 18° = 0·6263 (water = 1). Isopentane boils at 30°, sp. gr. at 18° = 0·628. Both are colourless, very mobile liquids, somewhat similar to chloroform, miscible with ether and alcohol in every proportion, solvents for fats; they burn with a brilliant white flame.

Hexane, C_6H_{14}.

Syn. caproylic hydride. Five isomers; the normal one occurs in petroleum, boghead- and cannel-tar; it is the principal constituent of the most volatile petroleum-ether (gasoline). Boils at 66-71°; sp. gr. at 17° = 0·663. Colourless, mobile liquid, of faintly ethereal smell, insoluble in water, miscible with ether, alcohol, acetone, etc. (this solubility holds good for all the higher members as well). Burns with a bright, luminous flame.

Warren found another hexane in petroleum, boiling at 61°·3, which Schorlemmer could not discover in that substance.

Heptane, C_7H_{16}.

Syn. œnanthylic hydride. Nine isomers possible. The different tars contain the normal one, boiling at 98°, sp. gr. at 0° = 0·7006, at 15° = 0·6886; also ethylisoamyl, boiling at 90°·3, sp. gr. at 0° = 0·6969. Mobile liquids, of faint, pleasant smell; burn with a somewhat smoky flame.

Octane, C_8H_{18}.

Syn. caprylic hydride, dibutyl, valyl. Of the eighteen possible isomers, one boiling at 119° or 120° (sp. gr. at 17° = 0·719), and another, probably the normal one, boiling at 124° (sp. gr. at 0° = 0·7188), have been found in petroleum, boghead- and coal-tar. Ahrens[1] found an octane in the oils distilling after the nitration of toluene, boiling at 121° to 122°, sp. gr 0·7245 at 23° C. They are limpid liquids with an ethereal smell and somewhat burning taste. The ordinary petroleum-spirit (benzoline) of commerce contains principally heptane and octane.

Nonane, C_9H_{20}.

That found in petroleum boils according to Wurtz at 130° to 132° (sp. gr. at 6° = 0·7242, smell like oranges); according to Beilstein at 150°·8. Which is right? Refined petroleum (kerosene) contains from C_9H_{20} up to $C_{16}H_{34}$, along with hydrocarbons of the formula C_nH_{2n}.

Decane, $C_{10}H_{22}$.

Syn. diamyl. Found in all tars, probably the isomer diisoamyl. Boils at 158° to 159°; at −30° it gets viscid; sp. gr. at 18° = 0·736. Beilstein states that the boiling-point is 161°, the sp. gr. at 16° = 0·757. O. Jacobsen[2] has found a decane, boiling at 170° to 171°, in the fractions of light coal-tar oil which pass over between 163° and 168°, along with pseudo-cumene and mesitylene.

Undecane, $C_{11}H_{24}$.

Found in American petroleum. Boils at 180° to 182°; sp. gr. at 16° = 0·765.

[1] *Ber.*, 1907, 848.

[2] *Ann. Chem.*, clxxxiv., p. 179.

Duodecane, $C_{12}H_{26}$.

Syn. dicaproyl, dihexyl, laurylic hydride. Found in bog-head-tar and petroleum. An oily, colourless liquid, with a pleasant, turpentine-like smell, boils at 200° to 202°; sp. gr. at at 18° = 0·7568; burns with a luminous flame without much smoke.

Higher members.

$C_{13}H_{28}$,	boiling-point	218-220°,	spec. grav.	0·778
$C_{14}H_{30}$	„	236-240°,	„	0·796
$C_{15}H_{32}$	„	258-262°,	„	0·809
$C_{16}H_{34}$	„	about 280°.		

Solid Paraffin

contains bodies of the formula $C_{17}H_{36}$ up to $C_{27}H_{56}$; also usually about 1 per cent. of oxygen. The paraffin found in the highest-boiling portions of real coal-tar is, according to Perkin, unlike ordinary paraffin; it fuses at a higher temperature, and is but slightly soluble in petroleum or naphtha. The proper paraffins occur principally in tar from Scotch and Lancashire cannel-coal.

Hydrocarbons of the Ethylene Series C_nH_{2n} (Olefins).

The lowest members of this series are gaseous at the ordinary temperature, but occur constantly in illuminating-gas, and probably dissolved in tar. The higher members are liquid; the highest solid. It is characteristic of all to unite directly with chlorine, bromine, or iodine, forming oily liquids; with bromine especially the reaction is very violent. This is ascribed to the circumstance that they are non-saturated compounds ("dyad radicals"), in which carbon occurs doubly tied, so that, when one of these ties is broken, two monovalent atoms can attach themselves directly; *e.g.*,

$$H_2C=CH_2 + Br_2 = BrH_2C-CH_2Br.$$
Ethylene + Bromine = Ethylene dibromide.

They also unite readily with the halogen hydrides HCl, HBr, and especially HI; also with hypochlorous acid, forming chlorhydrines, *e.g.*, $CH_2(OH)—CH_2Cl$. Concentrated sulphuric acids absorbs them, the lower members only at higher tempera-

tures, also by direct attachment and formation of sulphonic acids; *e.g.*,

$$H_2C = CH_2 + HO - SO_2 - OH = HO - SO_2 - OC_2H_5.$$
Sulphovinic acid.

From this it follows that these compounds can be removed from the tar-oils by bromine or by concentrated sulphuric acid. In ordinary coal-tar they play but an insignificant part; but they occur copiously in cannel- and boghead-tar.

Ethylene, C_2H_4.

Syn. elayl. Liquefies at 0° only under a pressure of 42½ atmospheres, at −110° under the ordinary pressure. Sp. gr. 0·9784. Water at 0° dissolves 0·25 vol.; at 15°, 0·16 vol. Much more dissolves in alcohol, ether, oil of turpentine, petroleum (about 2½ vols.), hence probably also in tar-oils. Concentrated sulphuric acid absorbs it on prolonged agitation, better at 160° to 175° C.; fuming oil of vitriol much more quickly, with formation of ethionic acid. Armstrong and Miller[1] have found it in the "hydrocarbon" condensed from Pintsch gas, as well as propylene, normal amylene, normal hexylene, and normal heptylene.

Propylene, C_3H_6.

Syn. tritylene. Not yet liquid at −140°, possessing an alliaceous smell. One hundred vols. of water dissolve at 0 44 vols., at 15° 23 vols.; absolute alcohol 12 to 15 vols., glacial acetic acid 5 vols. Its chemical behaviour is similar to that of ethylene.

Butylene, C_4H_8.

Syn. tetrylene, ditetryl. Three isomers are possible and known. First condensed by Faraday from the lighting-gas obtained from fatty oils, by strong pressure. Normal butylene,

$$CH_3 - CH_2 - CH = CH_2,$$

boils at −5°; pseudobutylene,

$$CH_3 - CH = CH - CH_3,$$

[1] *Journ. Chem. Soc.*, xlix., p. 74.

at $+1°$; isobutylene,

$$(CH_3)_2C=CH_2,$$

at $-7°$ or $-8°$.

Normal butylene has been obtained from the light oils of the compressed gas from boghead-coal by Brochet (*Comptes rend.*, cxiv., p. 601). In the first runnings of coal-tar it has been found by Ahrens (*Chem. Centr.*, 1906, 1, 510).

Amylene, C_5H_{10}.

Syn. pentylene, valerene. Of the five possible isomers, only that is well known which is obtained from amylic alcohol by water-abstracting reagents, especially zinc chloride. Whether this is identical with the amylene found in coal-tar,[1] and much more abundantly in boghead-tar, petroleum, etc., or not, is not quite certain; but it is usually assumed to be the same. At all events several amylenes occur in tar, probably also polymers (*cf.* Brochet, *loc. cit.*).

Ordinary amylene is a limpid, mobile liquid, of cooling, astringent, and somewhat pungent taste, and smelling somewhat like rotten cabbages. Its boiling-point is variously stated at from 33° to 42° (that obtained from amylic alcohol boils at 39°). Sp. gr. at $10°=0{\cdot}6549$. It is but sparingly soluble in water, but indefinitely miscible with alcohol. Like its congeners it unites directly with Cl, Br, HCl, HBr, HI, also with NO_2 and HOCl. Oxidising substances (potassium permanganate, chromic acid, etc.) convert it into fatty acids, carbon dioxide, ketons, etc. With sulphuric acid, Berthelot says,[2] it yields an acid isomer to sulphamylic acid, which Erlenmeyer[3] could not find. However this may be, all the isomers dissolve in sulphuric acid at ordinary temperatures, some of them even when it is not fully concentrated.

Amylene was used for some time as an anæsthetic, in lieu of chloroform.

Hexylene, C_6H_{12}.

Syn. caproylene. Of the many isomers, tar seems to contain essentially the normal, the only one pretty well known;

[1] Helbing, *Annalen*, clxxii. p. 281. Ahrens, *Chem. Centr.* 1906, 1, 510. Watson Smith (priv. comm.) has also found amylene in the first runnings of London tar, together with carbon bisulphide.

[2] *Comptes rend.*, lvi., p. 1242. [3] *Z. für. Chemie*, 1865, p. 362.

but other isomers are probably present as well (*cf.* Brochet, *loc. cit.*). Normal hexylene is a colourless, mobile liquid, smelling like amylene, boiling at 68-70°; sp. gr. at 0° = 0·6996; insoluble in water, readily soluble in ether and alcohol; chemically quite analogous to amylene. Sulphuric acid, diluted with $\frac{1}{3}$ vol. water, dissolves in the cold its volume of hexylene, from which mixture secondary hexylic alcohol soon separates. Concentrated sulphuric acid colours it reddish brown, gives off SO_2, and turns it into a thick oil.

Heptylene, C_7H_{14}.

Syn. œnanthylene. Like the above, found in boghead-tar. A limpid, mobile liquid with an alliaceous smell. Boils at 94° (Pelouze and Cahours), 96° (Schorlemmer), 99° (C. G. Williams). Sp. gr. at 18° = 0·718 (C. G. Williams), at 17·5° = 0·7388 (Schorlemmer). Its chemical behaviour is like that of the two foregoing compounds.

Aromatic Addition-products, C_nH_{2n}.

According to Beilstein and Kurbatow,[1] the hydrocarbons of Caucasian petroleum having the formula C_nH_{2n} are not identical with the compounds of the preceding series; such occur also in American petroleum along with heptane, etc. They were found identical with the hydrogen addition-products of aromatic hydrocarbons discovered by Wreden,[2] viz.:—

		Sp. gr. at 0°.	Boils at
Hexahydrobenzene .	C_6H_{12}	0·76	69° C.
Hexahydrotoluene .	C_7H_{14}	0·772	97° „
Hexahydroisoxylene .	C_8H_{16}	0·777	118° „

Schützenberger and Ionine,[3] who confirmed the above, proposed the name *paraffenes* for these compounds, inactive towards bromine, sulphuric acid, and nitric acid. Armstrong and Miller[4] found these saturated hydrocarbons of the formula C_nH_{2n}, which they call "pseudolefines," in the "hydrocarbon" condensing from Pintsch gas.

[1] *Ber.*, 1880, pp. 1818, 2028.
[2] *Liebig's Annalen*, clxxxvii., p. 166.
[3] *Comptes rend.*, xci., p. 828.
[4] *J. Chem. Soc.*, xlix., p. 90.

Markownikoff,[1] without denying the existence of hexahydrobenzene, etc., declared that most of what has been taken for these compounds belongs to a new class of compounds, which he calls "naphthenes." Later on[2] he practically confirmed the views of Beilstein and Kurbatow. Engler and his co-operators[3] have found naphthenes in nearly all descriptions of petroleum, also in the products artificially obtained by distilling fatty matters under high pressure. Renard[4] found them in essence of rosin (*cf.* also Maquenne),[5] Heusler[6] in oils from lignite-tar.

The following papers refer to the same subject:—Baeyer (*Lieb. Ann.*, cclxxviii., p. 111); Zalinski (*Berl. Ber.*, 1895, p. 780); Reformatzki (*ibid.*, 1896, p. 214); Spindler (*ibid.*, 1891, p. 563); Konowalow (*ibid.*, 1898, p. 44).

Bruhn (*Chem. Centr.*, 1898, ii., p. 1083) denies that the naphthenes are hexahydrobenzenes; he regards them as derived from a ring of five carbon atoms (like cyclopentadiene, etc.).

A good synopsis of our present knowledge of these products is given by Wischin in *Chem. Zeit.*, 1899, pp. 916 *et seq.*

The naphthenes are colourless liquids, smelling slightly like petroleum, hardly changing on standing in contact with air, completely oxidised by the ordinary oxidising agents. They are substituted by bromine only at higher temperatures, similar to the paraffins, from which they differ in the higher specific gravity of the compounds containing the same number of carbon atoms. Engler and Schneider have based upon this a method for distinguishing naphthenes and paraffins by their respective refractive indices.

Hydrocarbons of the Acetylene Series, C_nH_{2n-2}

Acetylene itself, C_2H_2, is a gas, and can only be dissolved in very small quantity in tar. Schorlemmer[7] has found in the light oil from cannel-coal, after treatment with sulphuric acid

[1] *Ann. Chem. Pharm.*, ccxxxiv., p. 89.
[2] *Berl. Ber.*, xx., p. 1850.
[3] *Dingl. polyt. J.*, cclxxi., p. 515.
[4] *Ann. Chim. Phys.* [6], i., p. 223.
[5] *Comptes rend.*, cxiv., pp. 918 and 1066.
[6] *Berl. Ber.*, 1895, p. 488.
[7] *Chem. News*, xiii., p. 253.

polymers of the acetylene series having the general formula $(C_nH_{2n-2})_2$, viz. :—

$C_{12}H_{20}$	boiling at	210° C.
$C_{14}H_{24}$	„	240° „
$C_{16}H_{28}$	„	280° „

They are colourless oily liquids, lighter than water, smelling like carrots or parsnips. They unite directly with bromine with a violent reaction; in concentrated nitric acid they dissolve; and on diluting the solution with water, oily nitro-compounds separate. Since the original oils boiled below 120° they cannot have contained these bodies, but those of the acetylene series, C_nH_{2n-2}, itself. In coal-tar they probably play even a less important part than in cannel-tar. But to acetylene itself a very important function in the formation of aromatic hydrocarbons is ascribed (see below, p. 178).

Allylene, C_3H_4.

Normal allylene, $CH_3-C{\equiv}CH$, discovered in 1861 by Sawitsch and by Markownikoff. Colourless gas, smelling like acetylene, soluble in water and especially in alcohol.

Isoallylene, $CH_2=C=CH_2$, discovered in 1872 by Aarland.

The allylenes have not yet been proved to exist in coal-tar; but they most probably do occur and play an important function like that of acetylene.

Crotonylene, C_4H_6.

Discovered in 1863 by Caventou; since then prepared synthetically and found in coal-tar[1] and in Pintsch tar.[2] Possibly the latter is isomeric with the crotonylene from coal-tar, and is not a true acetylene, $C_2H_5 . C{\equiv}CH$, or else dimethylene-ethane, $CH_2=CH-CH=CH_2$, or else dimethyl-acetylene, $CH_3 . C{\equiv}C . CH_3$.

Hydrocarbons of the Series C_nH_{2n-4}.

One such, *nonone*, C_9H_{14}, the next lower homologue of oil of turpentine, has been found by Tawildarow[3] in tar, viz. in

[1] Caventou, *Bull. Soc. Chim.* [2], xix., p. 245; Helbing, *Annalen*, clxxii., p. 281.

[2] Armstrong and Miller, *J. Chem. Soc.*, xlix., p. 80.

[3] *Z. für Chemie* [2], 1868, iv., p. 278.

the portion distilling after cumene, between 175° and 190°. On fractionating, most came over at 174°. This body does not appear to have been obtained in a pure state, and its existence cannot be considered completely established. It is possibly identical with Baeyer's synthetically prepared *dihydrocymene* (*Berl. Ber.*, 1893, p. 232).

Roscoe,[1] in "first runnings" from coal-tar, discovered a compound spontaneously formed by polymerization of the fraction boiling at 30°, and exhibiting the composition $C_{10}H_{12}$, melting at 32°·9. He considers it possible that this may have been formed from *valylene*, C_5H_6, but a search for that body proved unsuccessful. Etard and Lambert,[2] as well as Kraemer and Spilker,[3] proved that hydrocarbon not to be valylene, but pyropentylene or cyclopentadiene. Brochet, however,[4] isolated true valylene or "piperylene" from the compressed oil from boghead or schist, boiling at 41° or 42°.

Hexoylene, C_6H_{10}.

Syn. diallyl. A colourless liquid, with a penetrating alliaceous smell, boiling at 76° to 80°; sp. gr. at 13° = 0·71.

Cyclopentadiene, C_5H_6.

Syn. pyropentylene. Obtained in an impure state by Roscoe, in a pure state by Etard and Lambert (see above) from the condensation-products of oil-gas. Boils at 42°·5, sp. gr. 1·803. Kraemer and Spilker (see above) obtained it also from the first runnings of coal-tar benzol; they state the boiling-point = 41°, sp. gr. at 15° = 0·815.

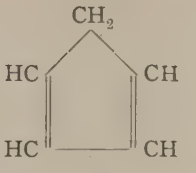
It has a peculiar smell; it is insoluble in water, but miscible in all proportions with alcohol, ether, and benzene. Concentrated sulphuric acid carbonises it with explosive violence; dilute acid causes it to "resinify." Chlorine, bromine, and iodine easily form addition-products; also aqueous sulphurous acid, the latter forming a compound $C_{10}H_{12},2H_2SO_3$, soluble in alkali, but insoluble in nearly all other reagents. Silver nitrate is at once reduced.

Cyclopentadiene polymerizes even in the cold quite spon-

[1] *J. Chem. Soc.*, xlvii., p. 669.
[2] *Comptes rend.*, 1891, cxii., p. 945.
[3] *Berl. Ber.*, 1896, p. 552.
[4] *Comptes rend.*, cxiv., p. 601.

taneously to a solid, *dicyclopentadiene* $(C_5H_6)_2$, which exhibits all the essential properties of oil of turpentine; boiling-point 170°.

Extensive investigations on cyclopentadiene have been made by I. Thiele.[1] The structural formula of cyclopentadiene is:



Hydrocarbons of the Benzene Series, C_nH_{2n-6}.

The compounds of this series, which commence the large class of the so-called aromatic compounds, are specifically characteristic of coal-tar. They occur also in the tar from wood, browncoal, shale, etc., but therein occupy a subordinate position.[2] But they are also formed by many reactions; above all by the action of heat, partly from their own higher homologues or other derivatives, partly by the decomposition or by the molecular condensation of aliphatic compounds. By the action of high temperatures, *e.g.*, by passing the vapour through red-hot tubes, benzene is formed not merely from toluene, xylene, styrolene, etc., but also from alcohol, acetic acid, ethylene, methane, frequently together with naphthalene; *e.g.*—

$$4C_7H_8 = 3C_6H_6 + C_{10}H_8 + 6H.$$

Of course, even more highly condensed molecules, such as anthracene, phenanthrene, chrysene, etc., are formed in a similar way, hydrogen being eliminated. By passing the mixed

[1] *Berl. Ber.*, 1900, p. 666.

[2] Markownikoff (*Ann. Chem. Pharm.*, ccxxxiv., p. 89) has found in Caucasian petroleum large quantities of benzene, toluene, xylenes, pseudocumene, mesitylene, durene, isodurene, diethyltoluene, and other hydrocarbons of the formulæ $C_{11}H_{14}$, $C_{11}H_{12}$, $C_{12}H_{14}$, $C_{13}H_{14}$. If these discoveries, which are certainly in opposition to the assertions of all previous investigators, were confirmed, it would become doubtful how much of the aromatic hydrocarbons, found after passing petroleum residues through red-hot tubes, are newly formed, and how much was already pre-existent in the original substance.

vapours of benzene and toluene through red-hot tubes, Carnelly[1] obtained naphthalene, diphenyl, paratolylphenyl, orthoparadiphenyl, two methylene diphenylenes, phenanthrene, anthracene, paradiphenyl-benzene, a hydrocarbon $C_{32}H_{28}$, a liquid hydrocarbon fusing at 13° and boiling at 290° to 316°, two other liquid hydrocarbons (or mixtures of hydrocarbons) boiling at 359° to 383° and 404° to 427°, and solid black bitumen.

It thus becomes conceivable why (as stated on p. 17) destructive distillation at lower temperatures yields more of fatty bodies and less of permanent gases, at higher temperatures more of aromatic compounds and more of permanent gases, and why, by passing the heavy hydrocarbons of the fatty class (from wood-tar, shale-tar, petroleum, etc.) through red-hot tubes, benzene and its derivatives can be prepared on a large scale (pp. 141 *et seq.*).

We shall return to this subject when treating of the theory of the formation of tar.

Benzene, C_6H_6.

Syn. benzol (this word is now mostly used for the commercial mixture of benzene, toluene, etc., in varying quantity), phenylic hydride. Benzene was discovered in 1825, by Faraday, in the liquid separating from condensed oil-gas. Mitscherlich, in 1833, prepared it by the dry distillation of calcium benzoate, determined its empirical formula, and conferred upon it its present name; he also discovered nitrobenzene. The first discovery of benzene in coal-tar is claimed by Leigh, who states that his communication to that effect made to the British Association meeting in 1842 was by an oversight omitted in its Report.[2] At all events his observation remained unknown and sterile; and the credit of having, in 1845, distinctly recognized the presence of benzene in coal-tar, and proved it by transforming it into nitrobenzene and aniline, will not be denied to A. W. Hofmann.[3] The process for obtaining it in any quantity from coal-tar was worked out in his laboratory by one of his pupils, Charles Mansfield,[4] who carried out the process on the large scale and minutely described the principle of dephlegmation for separating

[1] *J. Chem. Soc.*, Nov. 1880, p. 701.
[2] *Monit. Scient.*, 1865, p. 446.
[3] *Ann. Chem. Pharm.*, liv., p. 204.
[4] B. P. No. 11260, of Nov. 11, 1847; *Q. J. Chem Soc.*, i., p. 244.

the various hydrocarbons; he distinctly pointed out that the apparatus employed in rectifying spirit might be employed for this purpose, even with greater advantage than for spirit of wine itself[1]—a suggestion usually, but erroneously, ascribed to E. Kopp, who first mentions it in 1860.[2] Mansfield fell a victim to his discovery. On the 17th of February 1854, he was occupied with the distillation of benzene on a somewhat large scale for the Paris Exhibition, when the liquid in the retort boiled over and took fire, burning him so severely that he died in a few days.

Benzene was formerly considered to be a special characteristic of coal-tar, but this is erroneous. Thus Markownikoff (*Chem. Zeit.*, 1902, p. 572; comp. also the footnote on p. 176) found it in several descriptions of petroleum. Graefe (*Chem. Centr.*, 1906, i., 1681) found as much as 23 g. per cbm. in the gases produced in the destructive distillation of Thuringian lignite.

Mansfield had already utilized the property possessed by benzene (first observed by Faraday), of crystallizing at 0°, for preparing it in a state of perfect purity. It is allowed to solidify in a freezing-mixture; the liquid portion is pressed out; and, if necessary, the operation is repeated. Hofmann[3] has shown that the crystals easily enclose mother-liquor, which causes the product to contain toluene. Hence he prescribes preventing the formation of large crystals and completely separating the mother-liquor by atmospheric pressure, for which purpose he describes a convenient laboratory-apparatus.

Benzene is formed, on the one hand, by synthesis (condensation) from acetylene and other fatty compounds of simpler molecular constitution (the synthesis of benzene by fusing metal hydrates with metal carbides from the subject of an Amer. P. 635017, by C. B. Jacobs), and, on the other, by the splitting-up of more complex compounds, both fatty and aromatic, in both cases by the action of strong heat. In sealed tubes it remains unchanged even when heated to 400° C. Hence it is one of the most stable organic compounds; but on passing through red-hot tubes it also is decomposed, more highly condensed hydrocarbons, especially diphenyl, being formed (Berthelot, Schulze,[4]

[1] Lecture at the Royal Institution, April 27, 1849.
[2] *Monit. Scient.*, 1870, vol. ii., p. 829.
[3] *Ber.*, 1871, p. 162. [4] *Annalen*, clxxiv., p. 201.

Schmidt,[1] Behr und von Dorp).[2] According to M'Kee (*J. Soc. Chem. Ind.*, 1904, p. 403) it begins to decompose at 438°, and at 700° C. it is already strongly dissociated. Passed through red-hot tubes together with ethylene, it yields styrolene, naphthalene, diphenyl, acenaphthene, anthracene, etc. (Berthelot), all of which must consequently be found in crude illuminating-gas and the tar therefrom.

Benzene is a colourless mobile liquid of peculiar smell. Its boiling-point is stated at 80° to 81° (Mansfield), 80°·4 at a pressure of 760 mm. (Kopp), 80°·1 (Warren), 80°·36 (Regnault) 80°·5 (Weger). Adrieenz[3] found that benzene prepared from tar boils at 80°·53 to 80°·62, that from benzoic acid at 80°·60 to 80°·67. The temperature of a boiling mixture of benzene and water is 68°·5, that of the mixed vapours 69°·1.[4] The vapour tensions of benzene and its homologues have been minutely investigated by Woringer (*Chem. Centr.*, 1900, ii., p. 531). At 0° it solidifies to a mass of crystals, which fuse at 4°·45 (Regnault) or 7° (Mitscherlich). The crystals are orthorhombic prisms, whose axes $a : b : c$ have the ratio 0·891 : 1 : 0·799.[5] Its specific gravity at 0° = 0·8991 (Kopp), at 15° = 0·884 (Mendelejeff); at 0° = 0·8957, at 15° = 0·8820 (Warren), at 15° = 0·885 (Weger). Its coefficient of expansion is stated by Kopp for the temperature $t°$ (between 11°·4 and 81°·4) to be

$$V_t = 1 + 0{\cdot}001171626t + 0{\cdot}000001277555t^2 + 0{\cdot}000000008064 8t^3.$$

Adrieenz gives the following table for the specific gravity of benzene (prepared from benzoic acid):—

Temp.	Spec. grav.	Volume.	Temp.	Spec. grav.	Volume.
Degrees.			Degrees.		
0	0·90023	1	45	0·85291	1·05550
5	0·89502	1·00582	50	0·84748	1·06228
10	0·88982	1·01169	55	0·84198	1·06924
15	0·88462	1·01764	60	0·83642	1·07637
20	0·87940	1·02367	65	0·83078	1·08370
25	9·87417	1·02979	70	0·82505	1·09123
30	0·86891	1·03603	75	0·81923	1·09898
35	0·86362	1·04238	80	0·81331	1·10696
40	0·85829	1·04887			

[1] *Ber.*, 1874, p. 1365. [2] *Ibid.*, 1873, p. 723. [3] *Ibid.*, 1873, p. 441.
[4] Naumann, *Ber.*, 1877, p. 142. [5] Groth, *Pogg. Ann.*, cxli., p. 31.

The specific gravity of benzene from tar-oil he found at 0° = 0·90122 and 0·90129.

The specific heat of benzene between 19° and 46° = 0·450 (Kopp). Its refraction-index[1] for the line A is 1·4593; for D it is 1·5050; and for H, 1·5307; Adrieenz gives 1·4957 at 15°·2 for D.

The molecular combustion-heat of benzene, at constant pressure, is = 779·5 calories;[2] its capillary constant at 15 = 83·65 mm.[3]

Special investigations on the inflaming points of benzene and other hydrocarbons have been made by Raikow (*Chem. Zeit.*, 1899, p. 145); Meunier (*ibid.*, 1900, p. 951); Holde (*Chem. Centr.*, 1899, ii., p. 546).

Microchemical investigations on benzene and the other coal-tar hydrocarbons have been made by Behrens (*Chem. Centr.*, 1901, i., p. 796).

We also mention the work of Kraemer and Spilker on distillation under pressure (*Ber.*, 1900, p. 2205), the reactions of W. Loeb (*Ber.*, 1901, p. 915), of Dimroth (*Pharm. Zeit.*, 1901, p. 302), of Sabatier and Senderens (*Chem. Centr.*, 1901, i., pp. 501, 817).

Benzene is not merely a most important substance for industrial purposes, but even more so for theoretical chemistry. The enormous array of aromatic compounds are all derived from benzene. It would appear almost impossible to find one's way through this interminable field, had not Kekulé's celebrated theory of the constitution of benzene brought light and order into it. It can be stated, without fear of contradiction, that without Kekulé's hexagon formula nothing like so many and so important aromatic compounds would have been discovered as there have been; his hypothesis is certainly one of the most fertile and suggestive that have ever been propounded in Chemistry.

Nearly all chemists agree with Kekulé in assuming that the six carbon atoms of benzene are united in a closed chain (nucleus), and that, of the four bonds of each atom, three are satisfied by other carbon atoms of the same nucleus, the fourth

[1] Gladstone, *J. Chem. Soc.*, 1870, vol. xxiii., p. 152.

[2] Stohmann, Kleber, and Langbein, *Berl. Ber.* (Ref.), 1889, p. 527.

[3] *Chem. News*, 1886, vol. liv., p. 306.

being satisfied by hydrogen atoms. But opinions differ as to the special kind of bond; and it does not seem appropriate here to enter into this theoretical discussion, which is not yet closed.

For the sake of simplicity, benzene is usually represented merely by the figure of a hexagon, and its derivatives by attaching the respective groups to the corners, whilst the empty corners are understood to be filled with hydrogen atoms.

Benzene is very little soluble in water, but sufficiently so to communicate its smell to it. It is easily soluble in alcohol, ether, wood-spirit, acetone, etc. It dissolves iodine, sulphur,[1] phosphorus (when hot), and (very easily) fats, ethereal oils, rosins, etc. It is easily inflammable, as well as its vapour, which necessitates great precaution in storing it in quantity. It burns with a strongly smoking flame. Ordinary coal-gas passed through benzene gains very much in illuminating-power; Berthelot even ascribes that of (Paris) lighting-gas principally to the benzene contained in it; whilst formerly substances of the ethylene series received the credit. This has been confirmed by the researches of Frankland, of Knoblauch,[2] etc., and is now pretty generally assumed to be correct. Even atmospheric air passed through benzene yields a mixture burning with a bright flame, upon which property Mansfield at that time (before the discovery of the aniline colours) founded his hopes of an industrial utilization of benzene. Frankland and Thorne[3] made a quantitative investigation of the illuminating-power of benzene when mixed in the state of vapour with non-luminous gases. With ozone it forms "ozobenzol," a compound of fearfully explosive properties (Harries and Weiss, *Ber.*, 1904, p. 3431).

Benzene, on being inspirated in breathing, causes first a quickening of the pulse and the respiration, afterwards stupefaction, and in large doses (*e.g.*, 50 g. for a cat), it produces death. A case of this kind is reported in *Chem. Zeit. Rep.*, 1908, p. 39). In the case of men, the inspiration of 10 grammes benzene causes headache, giddiness, inclination to vomiting, coughing, and sleepiness. Forty to 50 grammes produce

[1] The somewhat considerable solubility of sulphur in benzene and ether (also the heavy tar-oils) has been studied in detail by E. Pelouze, junior (*Comptes rend.*, lxviii., p. 1179, lxix., p. 56).

[2] *Ber.*, 1881, p. 240.

[3] *Chem. News*, xxxvii., pp. 36, 72.

anæsthesia, similar to that produced by chloroform, with violent perspiration, sometimes with all the appearances of drunkenness. The workmen often complain of "ant-creeping" and dryness of the skin, owing to the oily secretions of the skin being dissolved. Nevertheless the men working in india-rubber works, and continually exposed to benzene vapours, enjoy normal health.

There are some contradictions on the point of the toxic quality of the tar hydrocarbons. Berthelot (*Comptes rend.*, cxxxvii., p. 953; *Chem. Centr.*, 1904, p. 1527) asserts that benzene, toluene, and xylene have very poisonous effects, whilst naphthalene has not. But Staehelin (*Chem. Centr.*, 1904, i., p. 1024) contends that only the vapours of benzene, not those of toluene or xylene, by themselves cause death, and that traces of such vapours form the principal poisonous constituent of coal-gas.

The changes undergone by benzene when passed through red-hot tubes have been mentioned above (p. 178).

Concentrated sulphuric acid at the ordinary temperature acts very little upon benzene, for which reason the latter can be purified by treatment with that acid. Even then, ordinary benzene contains some thiophen (see below), which can be removed by more energetically agitating with strong sulphuric acid till the "indophenine reaction"—that is, a blue colour imparted to isatin—is no longer obtained (V. Meyer). But on heating the mixture benzene-monosulphonic acid ($C_6H_5.SO_3H$) is formed, and at very high temperatures, or more easily by fuming sulphuric acid, benzene-disulphonic acid ($C_6H_4(SO_3H)_2$). Concentrated nitric acid converts benzene into nitro-compounds (mono- and dinitrobenzene), upon which its detection, its estimation, and, to a great extent, its industrial application are based. Oxidizing reagents, such as potassium permanganate, manganese dioxide, chromic acid, etc., act upon it but little, and with formation of complex products. About the action of ozone, see p. 181. Chlorine and bromine yield with it addition and substitution products. The action of fuming hydriodic acid under pressure furnishes hexahydrobenzene.

Benzene is a good indicator in iodometry, better than starch; *cf.* Schwerow (*Chem. Centr*, 1905, i., 1046), and Margosches (*ibid.*, ii., 510).

The methods for estimating benzene vapour in coal-gas have been described (pp. 55 *et seq.*); those for testing liquid benzene will be described in Chapter XI.

Toluene, $C_7H_8 = C_6H_5 . CH_3$.

Syn. methylbenzene. Toluene was discovered, in 1838, by Pelletier and Walter, in the condensation-products from the manufacture of rosin-gas, and was called "retinaphtha." Afterwards Deville obtained it by destructive distillation of tolu balsam; the name of toluene (toluol) was given to it by Berzelius. Mansfield found it in coal-tar, and it has since been met with in many mineral oils, *e.g.*, in petroleum by Charitschkoff (*Chem. Zeit. Rep.*, 1902, p. 179). Its formation, together with that of analogous compounds, has been mentioned above. It is obtained from coal-tar in very large quantities, and if necessary in a state of great purity, and is largely employed, partly for the manufacture of colouring-matters, partly as a solvent. It is more difficult to prepare in a perfectly pure state than benzene, because it does not crystallize.

Our present chemical theories admit only one toluene; and in fact it has been proved by Berthelot [1] and Rosenstiehl [2] that all toluenes, whatever be their origin, are identical.

Toluene is a colourless, mobile, strongly refractive liquid. Its boiling-point is 110° (Wilson), or 111° (Wilbrand and Beilstein), or 110°·3 (Warren). It does not solidify at −20°. Its specific gravity at 0° = 0·8824, at 15° = 0·8720 (Warren); or at 0° = 0·8841, at 15° = 8702 (Louguinine). The latter states its volume at the temperature t, if at 0° = 1, as

$$V_t = 1 + 0{\cdot}001028t + 0{\cdot}0000017796t^2.$$

Deville gives 1·4899 as its refraction-index. The capillary constant at 15° is = 83·95 mm. (Cohen, *Chem. News*, liv., p. 306).

The smell of toluene is rather different from that of benzene. It is insoluble in water, but communicates its smell to it; it is miscible with alcohol, ether, carbon bisulphide, etc. It dissolves sulphur, phosphorus, iodine, fats, etc. When ignited, it burns with a bright and strongly smoking flame. Passed through red-hot tubes it yields benzene, naphthalene, anthracene, phenanthrene, etc.

[1] *Bull. Soc. Chim.*, 1869, xi., p. 381. [2] *Ibid.*, xi., p. 385.

According to Berthelot, toluene possesses, similarly to oil of turpentine, the property of rendering oxygen active; when toluene is shaken up with a very dilute tepid solution of indigo in the presence of air, decolorization takes place.

Concentrated sulphuric acid dissolves toluene on heating and prolonged shaking; fuming acid does so much more quickly. In this two isomeric sulphonic acids are formed. Nitric acid of less than 1·42 sp. gr. does not act upon it when cold; but fuming nitric acid does so violently, even more so than upon benzene, nitro-products up to trinitrotoluene being formed. Oxidizing agents (dilute nitric acid, chromic acid, potassium permanganate) convert it into benzoic acid, but only with difficulty and great loss, so that this direct oxidation is scarcely practised on an industrial scale.

Xylenes, $C_8H_{10} = C_6H_4(CH_3)_2$.

Syn. dimethylbenzene. Xylene (*i.e.*, a mixture of the isomers) was discovered in 1850, by Cahours, in crude wood-naphtha. In coal-tar it was found by Ritthausen and Church; by Mabery in Californian crude petroleum. Latterly it has been synthetically produced by Friedel and Crafts, by treating benzene or toluene with methylic chloride in the presence of aluminium chloride.

Fittig first proved in 1869[1] that coal-tar xylene is not a homogeneous body; he stated it to contain 90 per cent. meta-xylene and 10 paraxylene. But O. Jacobsen[2] has proved the presence of orthoxylene, and estimates the proportion at 70 to 75 per cent. metaxylene, 20 to 25 paraxylene, and 10 to 16 orthoxylene; in any case different tars will differ in this respect (*cf.* Chapter XII.).

Crude xylene—that is, xylene which has not been treated with sulphuric acid (by which considerable quantities of ortho-xylene are dissolved)—probably contains much more orthoxylene than was found by Jacobsen in the refined article analyzed by him. This supposition (suggested by me in the first edition of this work, p. 44) has been confirmed by Jacobsen,[3] who found up to 25 per cent. of orthoxylene in crude coal-tar xylene.

Orthoxylene, $C_6H_4\begin{matrix}-CH_3\ (1)\\ -CH_3\ (2)\end{matrix}$, is a colourless liquid, whose

[1] *Annalen*, cliii., p. 265. [2] *Ibid.*, 1877, p. 1009. [3] *Ber.*, 1881, p. 2628.

pleasant aromatic smell differs from that of its isomers. It boils at 141° to 142°, and is not yet solid at −22°. It dissolves in concentrated sulphuric acid, forming a sulphonic acid. Dilute nitric acid forms orthotoluylic acid, fusing at 102°; potassium permanganate forms phthalic acid; chromic acid entirely burns it up. The sulphochloride melts at 52°, the sulphamide at 144°. Capillary constant = 86·95 mm. at 15° (Cohen).

Metaxylene (*syn.* isoxylene, $C_6H_4\begin{matrix}-CH_3\ (1)\\ -CH_3\ (3)\end{matrix}$, boils at 139°, is also soluble in concentrated sulphuric acid, two sulphonic acids being formed. Dilute nitric acid forms metatoluylic acid, of 106° fusing-point; potassium permanganate and chromic acid form isophthalic acid. There are two sulphochlorides, one melting at 34°, the other liquid; the two sulphamides melt at 137° and 96° respectively. Specific gravity of metaxylene = 0·8668 at 19°. Capillary constant at $15\frac{1}{4}° = 84·3$ mm. (Cohen).

Paraxylene, $C_6H_4\begin{matrix}-CH_3\ (1)\\ -CH_3\ (4)\end{matrix}$, melts at 15°, and boils at 137°·5 to 138.° Possesses an odour similar to that of orthoxylene, but with a faint smell of aniseed superadded. According to Glinzer and Fittig, its sp. gr. (not quite pure) at 18°·5 = 0·8625. Capillary constant at $15\frac{1}{4}° = 83·80$. It is very little acted upon even by hot concentrated sulphuric acid; but faintly fuming oil of vitriol dissolves it, forming a sulphonic acid which can be precipitated by water and purified by recrystallization, and from which by dry distillation pure paraxylene is regenerated. This behaviour shows how it can be isolated. Dilute nitric acid forms paratoluylic acid, melting at 178°; potassium permanganate and chromic acid form terephthalic acid. The sulphochloride melts at 26°, the sulphamide at 148°. The tar isomers dissolved in sulphuric acid can be separated in the following way (Jacobsen). As much as possible of the excess of sulphuric acid is removed by calcium carbonate; the liquid is mixed with a slight excess of sodium carbonate, and the filtrate evaporated so far that on cooling a considerable crop of salt is obtained. This sodium orthoxylene sulphonate can be purified by recrystallization, whilst the mother-liquors contain sodium metaxylene sulphonate. From these salts the hydrocarbons are obtained by dry distillation or by heating

with hydrochloric acid to 195°. Coal-tar xylene contains a body similar to paraffin, insoluble even in fuming oil of vitriol, which has been examined by Kraemer and Boettcher (*Ber.*, 1887, xx., p. 602) (*cf.* Levinstein's process in the twelfth chapter).

Trimethylbenzenes, $C_9H_{12} = C_6H_3(CH_3)_3$.

Mansfield originally discovered hydrocarbons of the empirical formula C_9H_{12} in coal-tar, but evidently did not isolate them in the pure state. Like him, other chemists for a number of years believed they had to deal with a homogeneous body, identical with the retinyl obtained in 1837 by Pelletier and Walter from rosin-oil or cumene (cumol propylbenzene), and procured by Gerhardt and Cahours from cuminic acid. Even xylene was frequently confounded with cumene. This confusion Beilstein[1] put an end to by describing the individual substance as *pseudocumene*. Already Warren[2] had obtained it in a similar state, boiling at 169°·8. But Fittig and his disciples[3] proved that Beilstein's pseudocumene is a mixture of two isomeric trimethylbenzenes, viz., that of pseudocumene as at present understood (1, 2, 4), and of mesitylene (1, 3, 5). K. E. Schulze (*Berl. Ber.*, 1887, p. 409) found in the fraction of neutral coal-tar oils boiling between 170° and 210° about 15 per cent. trimethylbenzenes. Besides them O. Jacobsen[4] has found a paraffin, $C_{10}H_{22}$, boiling at 170° to 171°. The same chemist has described[5] the preparation of both hydrocarbons in a pure state by converting them into their sulphamides, separating these by crystallizing from alcohol, and decomposing the sulphamides by heating them with hydrochloric acid to 175°.

Engler[6] has found both pseudocumene and mesitylene in different kinds of petroleum; so has Markownikoff (p. 176, note).

Pseudocumene, $C_6H_3\begin{cases}CH_3\ (1)\\CH_3\ (2)\\CH_3\ (4)\end{cases}$, boils at 169°·5.[7] Its smell differs from that of the lower homologues. It is insoluble in

[1] *Ann. Chem. Pharm.*, cxxxiii., p. 32.
[2] *Chem. News*, xii., p. 292.
[3] *Ann. Chem. Pharm.*, cxxxix., p. 184; cxlv., p. 137; cl., pp. 257, 283, 292.
[4] *Annalen*, clxxxiv., p. 179.
[5] *Ber.*, 1876, p. 256.
[6] *Ibid.*, 1885, p. 2234.
[7] O. Jacobsen, *Ber.*, 1886, p. 2513.

water, soluble in ether and alcohol, also in glacial acetic acid (like mesitylene). Treated with sulphuric acid it dissolves (like mesitylene) with formation of a sulphonic acid.

Mesitylene, $C_6H_3\begin{cases}CH_3\ (1)\\CH_3\ (3)\\CH_3\ (5)\end{cases}$, was discovered by Kane[1] by treating acetone with sulphuric acid. Fittig found it in coal-tar oil. Boils at 163° (Fittig); smells rather like garlic.

Hemellithol, $C_6H_3\begin{cases}CH_3\ (1)\\CH_3\ (2)\\CH_3\ (3)\end{cases}$, discovered by O. Jacobsen in 1882 (*Berl. Ber.*, 1882, p. 1857), and found by him in coal-tar oils in 1886 (*ibid.*, 1886, p. 2517); also by Krömer (*ibid.*, 1891, p. 2407) in commercial pseudocumidine. Boils at 175° to 175°·5, and does not solidify at −20°.

Weger[2] has found that cumene, as well as many unsaturated hydrocarbons in coal-tar, absorb oxygen from atmospheric air when kept in daylight; they then burn yellow and otherwise change their properties.

Ethylbenzene, $C_6H_5 . C_2H_5$.

This isomer of the xylenes has been found in technical coal-tar xylene by Noelting and Palmer[3] to the extent of 10 per cent., as the first representative among coal-tar oils of hydrocarbons with a prolonged lateral chain. Kraemer (priv. comm.) points out that ethylbenzene does not exist as such in coal-tar, no more than any other hydrocarbons with prolonged lateral chains, because these are split off during the heating in the tar-still. The ethylbenzene found by Noelting and Palmer must have been formed as secondary products from the paracumarone contained in the crude xylenes, *washed with strong sulphuric acid* from which the "technical xylene" had been obtained by distillation. It has been synthetically prepared by Brochet.[4] Colourless liquid, smelling like xylene, boiling-point 137°. Friedel and Crafts[5] describe a method for separating it from the benzenes by the bromine derivatives. The pentabromide of ethylbenzene appears in fine crystals; fusing-point 136°.

[1] *Poggend. Ann.*, xliv., p. 474. [2] *Ber.*, 1903, 309.
[3] *Berl. Ber.*, 1891, p. 1955; *Z. angew. Chem.*, 1909, p. 341.
[4] *Comptes rend.*, cxvii., p. 115. [5] *Ibid.*, ci., p. 1218.

Tetramethylbenzenes, $C_{10}H_{14}$.

K. E. Schulze[1] found the 1, 2, 4, 5 *Durene* in the fraction of tar-oil boiling between 180° and 200, after removing the bases and phenols. White scales, with a faint fluorescence, smelling similar to pseudocumene; fusing-point 80° to 81°, boils at 196°; sublimes with much more difficulty than naphthalene. Most probably other isomers are present in this oil, which occurs in coal-tar in nearly the same proportion as benzene.

He also obtained from 15 to 20 per cent. of these in the neutral fraction boiling between 170° and 210°.[2]

Naphthenes

have been proved to occur in coal-tar by Kraemer and Spilker,[3] and in lignite by Heusler.[4] Nononaphthene, C_9H_{18}, has been found by Ahrens and Modzenski (*Z. angew. Chem.*, 1908, p. 1411) in waste oil from the manufacture of nitro-xylene, and must have been originally in the coal-tar.

Styrolene, $C_8H_8 = C_6H_5 . CH = CH_2$.

Syn. cinnamene, vinylbenzene. Usually obtained from storax or Peru balsam; synthetically by Berthelot[5] by condensation of acetylene at the temperature of softening glass, or better, by passing a mixture of benzene and ethylene through red-hot and even better through white-hot tubes, thus:

$$C_6H_6 + C_2H_4 = C_8H_8 + H_2.$$

These and similar reactions explain the occurrence of styrolene in coal-tar, in which, however, it occurs only in insignificant quantities.[6]

It is a colourless mobile oil, with a strong aromatic smell, reminding one of benzene and naphthalene. It does not solidify at −20°, boils at 145°, but volatilizes at ordinary temperatures, so that it does not leave a grease-spot on paper.

[1] *Ber.*, 1885, p. 3032.
[2] *Ibid.*, 1887, p. 410.
[3] *Ibid.*, 1887, p. 595.
[4] *Ibid.*, 1895, p. 488.
[5] *Comptes rend.*, lxiii., pp. 481, 518, 792, 834; lxviii., p. 327.
[6] Berthelot, *Z. für Chemie*, 1866, 736; Kraemer and Spilker, *Berl. Ber.*, 1890, pp. 3169, 3269.

Sp. gr. at 16° = 0·876. Its solubilities are quite analogous to those of benzene. Caustic potash has no action upon it; fuming sulphuric acid converts it into a sulphonic acid, ordinary sulphuric acid only into a solid polymer, which, on distillation, is partly reconverted into styrolene. Chlorine and bromine unite directly with it. Fuming nitric acid dissolves it, forming a nitro-compound. At a red heat it splits up into benzene and acetylene,

$$C_8H_8 = C_6H_6 + C_2H_2,$$

or, if mixed with hydrogen, into benzene and ethylene,

$$C_8H_8 + H_2 = C_6H_6 + C_2H_4;$$

that is, the reaction is the inverse of that which took place in its formation. Heated with ethylene it yields benzene and naphthalene; heated with benzene, naphthalene, and anthracene. It probably plays an important part in the formation of these higher hydrocarbons, and, for that very reason, does not occur in large quantities in coal-tar. The investigations of Kronstein (*Ber.*, 1902, pp. 4150, 4153) on the polymerization of styrolene point in the same direction. According to Königs[1] it also condenses easily with phenols. A very complete investigation on styrolene has been made by Klages (*Ber.*, 1902, pp. 2245, 2633).

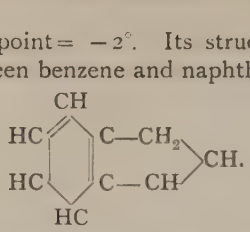
In the presence of sulphuric acid, styrolene forms molecular compounds with toluene, xylene, cumene, etc., which can be distilled without decomposing. On overheating their vapours methane and hydrogen are split off, and anthracene or its homologues are formed.

Indene, C_9H_9.

Discovered by Kraemer and Spilker[2] in the fraction of crude benzol boiling at 176° to 182°, which contains about 20 per cent. of it. Colourless liquid, boiling at 182°. On standing, it takes a yellowish-green colour, which vanishes in the light. They state the sp. gr. at 15° = 1·040, but Weyer, when examining a more purified substance, found it = 1·008. Spilker and Dombrowsky (*Ber.*, 1909, p. 573) found the boiling-point of really pure indene = 182°·2-182°·4 at 761 mm. pressure; sp. gr.

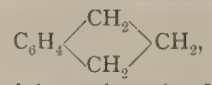
[1] *Ber.*, 1890, p. 3147. [2] *Ibid.*, p. 3276.

1·0002; solidifying-point = $-2°$. Its structural formula proves it to be a link between benzene and naphthalene:



Perhaps other formulæ or isomers must be assumed.[1]

Its hydrogenated derivative, *hydrindene*,



has been likewise found in coal-tar by Kraemer and Spilker.[2] These authors ascribe to indene the coloration produced by impure naphthalene, etc., in contact with concentrated sulphuric acid; perhaps also that of phenol. Dennstedt and Ahrens[3] have found it in the product condensed from ordinary coal-gas by cooling down to $-10°$. Special investigations on indene and hydrindene have been made by J. Thiele (*Ber.*, 1900, p. 771), Moschner (*ibid.*, 1900, p. 757), and Weger and Billmann (*Ber.* 1903, p. 640).

Methylindenes, $C_{10}H_{10}$, and *Dimethylindenes*, $C_{11}H_{12}$, have been found by Boes (*Chem. Centr.*, 1902, i., 811), in the fraction of coal-tar boiling at 220° to 230°. If all six possible dimethylindenes occur in coal-tar, the 4, 6 and 5, 7 isomer must occur in the greatest proportion. (*Cf.* also *Ber.*, 1902, p. 1762, and *Chem. Centr.*, 1902, ii., 55.)

Naphthalene, $C_{10}H_8$.

Discovered by Garden in 1826; first studied in detail by Laurent. It is formed in innumerable cases by the action of heat on organic substances, but only at rather high temperatures; so that tar obtained at a comparatively low heat does not contain it at all. In gas-tar it always occurs, but in greatly varying quantities, very much greater since the cast-iron retorts have been replaced by fireclay retorts worked at much higher temperatures. The statement of Calvert,[4] that Newcastle tar

[1] Perkin, jun., and Revay, *Ber.*, 1893, p. 2251; Dennstedt and Ahrens, *ibid.*, 1895, p. 1331.

[2] *Ber.*, 1896, p., 561. [3] *Ibid.*, 1894, p. 601. [4] *Comptes rend*, xlix., p. 262.

contains 58 per cent. of naphthalene, is absurd on the face of it; ordinarily tar seldom contains more than from 5 to 10 per cent. The mode of its formation has been explained on p. 178.

In the pure state it forms white crystalline masses or thin rhomboidal scales; on spontaneous evaporation of an ethereal solution it appears in monoclinic prisms (Laurent). It fuses at 79°; solidifying-point = 79°·6-79°·8 (Weger, *Z. angew. Chem.*, 1909, p. 341); the statements respecting its boiling-point vary between 212° and 220°; but 218° seems to be correct. Sp. gr. at 15° = 1·1517, at 18° = 1·158, at 79°·2 = 0·9778, at 100° = 0·9628 (compared with water at 0°). Melted naphthalene, according to Vohl,[1] absorbs a large quantity of air, which is given off again on cooling; it is said to be much richer in oxygen than atmospheric air. Naphthalene volatilizes far below its boiling-point, and distils both with aqueous vapour and with that of light tar-oils; hence it always appears with the latter in crude tar-oils. In an ammoniacal atmosphere it volatilizes more easily than in air, hydrogen, etc.[2] Even at ordinary temperatures it volatilizes slowly and gives off a penetrating tarry smell, which clings a long time to clothes, etc., and is said to keep off moths and other vermin. Ballo[3] asserts that this smell is not that of pure naphthalene, but of leucoline oil; however, the purest obtainable naphthalene exhales it quite strongly. Justin Mueller, according to *Chem. Zeit.*, 1905, p. 221, in that year communicated to the Société industrielle de Rouen the startling news that naphthalene, when spread in thin layers on glass or stone plates, volatilizes at ordinary temperatures! Its taste is pungent. Edlefoen (*Chem. Centr.*, 1905, ii., p. 1341) describes the action of naphthalene on the human organism when taken in small quantities. It burns with a strongly smoking flame, but its vapour mixed in small quantity with gas considerably enhances the illuminating-power of the latter. The heat of combustion of 1 g. naphthalene is 96,356 to 96,683 calories (Fries, *Chem. Centr.*, 1907, i., 510).

It is insoluble in cold[4] but not quite in hot water; so that the latter turns milky on cooling. It is easily soluble in

[1] *J. prakt. Chem.*, cii., p. 29. [2] Tieftrunck, *Ber.*, 1878, p. 1466.
[3] *Dingl. polyt. J.*, ccii., p. 377.
[4] Lupton (*Chem. News*, xxxiii., p. 90) doubts this, but does not adduce any positive proof to the contrary.

alcohol, ether, fatty and essential oils, and acetic acid, very much so in phenols, but less easily in the indifferent tar-oils. When melted, it dissolves phosphorus, sulphur, indigo, and several metallic sulphides, which crystallize on cooling. According to Bechi,[1] 100 parts of absolute alcohol at 15° dissolve 5·29 parts, at the boiling-point any quantity; 100 parts of toluene at 16°·5, 31·94 parts, at 100° any quantity. The quantitative estimation of naphthalene in coal-gas and in other cases will be described in Chapter IX.

Alkalis do not act very much upon naphthalene, but alkaline liquors dissolve a little of it. Concentrated sulphuric acid, on heating, converts it into sulphonic acids—below 70° principally into the α, at 160° almost entirely into the β modification. This behaviour is very important, because the corresponding naphthols can only be made from the proper sulphonic acids. Chlorine yields both addition and substitution products; nitric acid, nitronaphthalene.

The constitution of naphthalene has been elucidated chiefly by the researches of Laurent, later on by Erlenmeyer[2] and Graebe[3]; it is generally assumed to consist of two benzene nuclei, attached to each other by two carbon atoms.

In order to prove the presence of naphthalene, Vohl treats the substance in question with fuming nitric acid, adds a large quantity of water, washes the precipitated nitre-compound, and puts it into a boiling mixture of 1 part potassium monosulphide and 1 part caustic potash; traces of naphthalene yield a beautiful purple solution.

Naphthalene dihydride, $C_{10}H_{10}$.

Discovered by Berthelot[4] as a product of the action of concentrated hydriodic acid on naphthalene; occurs also in coal-tar. A viscid fluid, with a strong disagreeable smell, boiling at 200° to 210°. Is powerfully acted upon by bromine, and dissolves in cold fuming nitric acid. It has been studied in detail by Bamberger and Lodter.[5]

[1] *Ber.*, 1879, p. 1928.
[2] *Ann. Chem. Pharm.*, cxxxvii., p. 346.
[3] *Z. fur Chemie* [2], iv., p. 114.
[4] *Bull. Soc. Chim.*, 1868, ix., p. 287.
[5] *Berl. Ber.*, 1891, p. 1887, and 1893, p. 1833; *Annalen*, cclxxxviii., p. 74.

Naphthalene tetrahydride, $C_{10}H_{12}$,

occurs in small quantity together with the dihydride; it boils at 190°. Its other properties are similar to those of the latter body.[1] Boes (*Chem. Centr.*, 1902, ii., 1119) found that it absorbs oxygen very easily. He believes it to be identical with a hydrocarbon found by Graebe and Guye (*Ber.*, 1883, xvi., 3028), which absorbs oxygen from atmospheric air.

Methylnaphthalenes, $C_{11}H_{10}$.

Reingruber[2] found these in that portion of coal-tar which distils between 220° and 270°, and which remains liquid at ordinary temperatures; but the two isomeric methylnaphthalenes were only separated by K. E. Schulze (*Ber.*, 1884, p. 842). They are miscible in all proportions with absolute alcohol, ether, benzene, carbon bisulphide, and glacial acetic acid. Oxidizing agents act briskly upon them, and destroy them with evolution of carbon dioxide. The two isomers can be separated by means of their sulphonic acids.

α Methylnaphthalene is a colourless oil of aromatic smell, with strong refraction and with fluorescence. It solidifies at −22°, and boils at 240° to 243°; sp. gr. 1·005 at 19°.

β Methylnaphthalene crystallizes in scales somewhat like naphthalene, of rather pungent smell and burning taste; it melts at 32°·5, and boils at 241° to 242°.

The ordinary "creosote oil" of trade, which distils mainly between 200° and 300°, contains about 6 per cent. of these methylnaphthalenes, rather more of the β than of the α modification.

Dimethylnaphthalene, $C_{12}H_{12}$.

Emmert and Reingruber[3] found a body of this composition, boiling at 262° to 264°, in coal-tar. There are evidently several isomeric bodies of this formula, but so far it has not been found practicable to separate them.

Tammann (Ger. P. 95597; *Z. angew. Chem.*, 1898, p. 46) has prepared some new di-, tri-, and tetramethylnaphthalenes from petroleum and shale-oil.

[1] *Cf.* Bamberger and Bordt (*Ber.*, 1889, p. 631), Kraemer and Spilker (*ibid.*, 1896, p. 561), Kraemer and Boettcher (*ibid.*, 1887, p. 603).

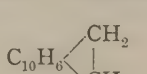
[2] *Annalen*, ccvi., p. 367. [3] *Ibid.*, ccxi., p. 65.

Phenylnaphthalenes, $C_{16}H_{12}$.

Most probably these occur in coal-tar, but they have been only synthetically isolated by Moehlau and Baeyer (*Berl. Ber.*, 1893, p. 1199) and Zincke and Breuer (*ibid.*, 1878, p. 1403).

Acenaphthene, $C_{12}H_{10}$,

occurs in that portion of coal-tar which boils at 270° to 300°, especially between 280° and 290°, and crystallizes on cooling. By recrystallizing from light tar-oil or alcohol, or cautious subliming, it is obtained pure.[1] It fuses at 95° and boils at 277°·5. Crystallized from alcohol, it forms long, colourless, shining needles; from heavy tar-oils it separates in hard, brittle crystals. Its smell resembles that of naphthalene. It is little soluble in cold, easily in boiling alcohol. Bromine acts readily upon it; concentrated sulphuric acid dissolves it, forming a sulphonic acid, of which all the salts are easily soluble; concentrated nitric acid forms a nitro-compound. Its constitution is—



Acenaphthene hydride, $C_{12}H_{12}$,

is stated by Berthelot to occur together with the preceding body in coal-tar. It boils at 260°. A perhydride, $C_{12}H_{20}$, has been obtained by Liebermann and Spiegel (*Ber.*, 1889, p. 779) as a colourless liquid, boiling at 235° to 236°.

Diphenyl, $C_{12}H_{10}$.

Discovered in 1862 by Fittig.[2] It occurs in that fraction of coal-tar which boils at from 220° to 270°;[3] this has been confirmed by K. E. Schulze (*Ber.*, 1885, p. 1203), who considers it also probable that higher homologues (methyldiphenyl) occur there as well. It fuses at 70°·5, and boils at 254°. It readily dissolves in alcohol and ether, and crystallizes in large colour-

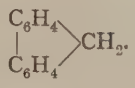
[1] Berthelot, *Ann. Chim. Phys.* [4], xii., p. 226.
[2] *Ann. Chem. Pharm.*, cxxi., p. 361.
[3] Fittig and Büchner, *Ber.*, 1875, p. 22.

less scales. Bromine, sulphuric acid, and nitric acid act upon it, and form corresponding derivatives. Its rational formula is

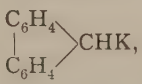
Diphenyl hydrides have been prepared by Bamberger and Lodter (*Ber.*, xx., p. 3077).

Fluorene, $C_{13}H_{10}$.

Syn. diphenylene-methane. Prepared by Berthelot[1] from coal-tar, synthetically by Graebe, Fittig, and others in various ways; specially examined by Barbier.[2] It is obtained from the fraction of coal-tar boiling between 290° and 350°, after naphthalene and anthracene are separated by fractional distillation; the portion distilling between 295° and 310° is purified by repeated recrystallization from alcohol. It forms colourless scaly crystals with a violet fluorescence, little soluble in cold, easily in hot alcohol, also in ether, benzene, and carbon bisulphide. Fuses at 116° (Weger), boils at 295°, but volatilizes with aqueous vapour. Bromine and nitric acid yield derivatives with it. The rational formula is



Weissgerber (*Ber.*, 1901, p. 1659) showed that fluorene has a slightly acid character. When fused with caustic potash at 270° to 290° C., it forms a compound of the formula



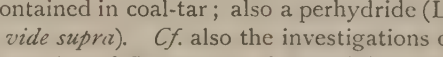
and by this means it can be obtained in the pure state from the high-boiling fractions of coal-tar, as the melt thus formed can be mechanically separated from the non-attacked hydrocarbons, and on being treated with water, is split up into KOH and regenerated fluorene. The Akt. Ges. f. Teer- u. Erdöl-Industrie has patented this process (Ger. P. appl. A7302). According to a more recent patent of Weissgerber's, the *sodium* compound is

[1] *Comptes rend.*, lxv., p. 465. [2] *Ibid.*, lxxvii., p. 442; lxxix., p. 1151.

preferable to the potassium compound for the purification of fluorene on account of the lower fusing-points.

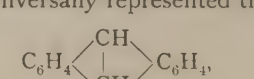
There is a series of isomers of this formula[1] which are probably partly contained in coal-tar; also a perhydride (Liebermann and Spiegel, *vide supra*). *Cf.* also the investigations of J. Thiele (*Ber.*, 1900, p. 851), and Stoermer and Boes (*Ibid.*, 1900, p. 313).

Fluorene forms a natural series with cyclopentadiene and indene:



Anthracene, $C_{14}H_{10}$.

Discovered by Dumas and Laurent in 1832, and described as *paranaphthalene;* more especially examined in 1857 by Fritzsche, who was the first to find it in coal-tar.[2] This was confirmed by Anderson's extended investigation in 1862. Anderson also established the correct formula of anthracene. Synthetically it was first prepared by Limpricht[3] in 1866, from benzylic chloride, in the same year by Berthelot, pyrogenetically, from simpler hydrocarbons. The most important epoch in its history was marked by Graebe and Liebermann's discovery, in 1868, that it is formed from alizarin by the reducing action of zinc dust, and that alizarin can be synthesized from it.[4] The same chemists established the structural formula of anthracene, but first gave it that now generally ascribed to phenanthrene. Anthracene is now universally represented thus:



i.e., two benzene nuclei, connected by two carbon atoms which are united with each other by another bond. It is also now ascertained that both bonds are in the ortho-position towards the benzene nuclei.

Anthracene is formed in many cases when organic bodies are subjected to a great heat, not merely in the dry distillation of coal, but also when passing the vapours of petroleum,

[1] Carnelley, *J. Chem. Soc.*, Nov. 1880, p. 701; Lunge and Steinkauler, *Ber.*, 1880, p. 1656.

[2] *J. prakt. Chem.*, lxxiii., p. 286.

[3] *Ann. Chem. Pharm.*, cxxxix., p. 308.

[4] *Ber.*, 1868, p. 49.

browncoal-tar, wood-tar, benzene, spirits of turpentine, etc., through red-hot tubes.

The mode of its formation from other hydrocarbons is illustrated by the following equations, which may serve as examples :—

$$\underset{\text{Toluene.}}{2C_7H_8} = C_{14}H_{10} + 6H,$$

$$\underset{\text{Naphthalene+Acetylene.}}{C_{10}H_8 + 2C_2H_2} = C_{14}H_{10} + 2H,$$

etc. etc.

It has been synthetically obtained from toluene-styrene by Kraemer and Spilker (*Ber.*, 1890, pp. 3169 and 3269); other syntheses are those by Behr and Van Dorp (1874), Perkin and Hodgkinson (1874), Paternò and Fileti (1874), Jackson and White (*Amer. Chem. J.*, ii., p. 283), Auschütz and Eltzbacher (1883), and Delaire (1885).

Köhler[1] found 35 per cent. anthracene in a product accidentally formed by a violent reaction on overheating the higher-boiling fractions of crude carbolic acid, although that product had been obtained from "light oil," and could hardly contain substances which would yield anthracene by a mere splitting-off of the elements of water. He regarded this as a confirmation of K. E. Schulze's theory of the formation of the hydrocarbons of tar from phenols, and also of the statement that the anthracene of coal-tar is for the most part formed during the process of distillation itself; but this view cannot be maintained in face of the smooth synthesis from toluene-styrene by Kraemer and Spilker. Kraemer (priv. comm.) states that the above observation cannot be correct; by overheating phenol mere traces of anthracene are formed.

Anthracene has also been found in that peculiar greasy substance called "stupp," which is formed in the distillation of mercury from its ores (G. Goldschmidt and M. von Schmidt).

Its preparation from the highest-boiling constituents of coal-tar, and the analysis of crude anthracene, will be minutely described in a separate chapter later on (Chapter VII.). The preparation of *chemically pure anthracene* (which is not a commercial article) is not easy, unless crude anthracene distilled over caustic potash can be employed. From this, by

[1] *Ber.*, 1885, p. 859.

one washing with carbon disulphide and several recrystallizations from petroleum spirit, pyridine or benzene, beautiful white scales with blue fluorescence are obtained, which it is very difficult to obtain from ordinary crude anthracene. This is best accomplished after subliming at the lowest possible temperature and washing with ether to remove yellow colouring-matters; or it is dissolved in benzene and bleached by sunlight, in which case a little paranthracene is always formed. The safest way to obtain chemically pure anthracene is to reduce its derivatives by zinc-dust.[1]

Pure anthracene forms shining white scales (clinorhombic prisms) with violet fluorescence. It fuses at 210° (Fritzsche, Berthelot), or 213° (Graebe and Liebermann), or 216°·5 (Reissert, *Ber.*, 1890, p. 2245), and sublimes at about the same temperature, with a pungent smell, yielding small, mica-like scales. At about 360° (certainly above phenanthrene) it boils and yields a yellowish-white crystalline distillate; a portion, however, is always decomposed. In the cathode-light vacuum it sublimes already at 103° to 104° (Krafft and Weylandt, *Ber.*, 1896, p. 2240).

Pure anthracene is insoluble in water, little soluble in alcohol, more so in ether, benzene, and essential oils, as well as in boiling alcohol, and especially in light tar-oils. According to Gessert,[2] 100 parts of

Alcohol, cold	.	dissolve 0·6	of anthracene
Benzene .	.	„ 0·9	„
Carbon disulphide		„ 1·7	„

According to Versmann,[3] at 15° 100 parts of

Alcohol, sp. gr. 0·800,		dissolve 0·591	of anthracene
„	„ 0·825,	„ 0·574	„
„	„ 0·830,	„ 0·491	„
„	„ 0·835,	„ 0·475	„
„	„ 0·840,	„ 0·460	„
„	„ 0·850,	„ 0·423	„
Ether .	. .	„ 1·175	„
Chloroform	. .	„ 1·736	„
Carbon disulphide	.	„ 1·478	„
Glacial acetic acid	.	„ 0·444	„
Benzene .	. .	„ 1·668	„
Petroleum .	. .	„ 0·394	„

[1] Auerbach, *Das Anthracen*, 2nd ed., p. 12.

[2] *Dingl. polyt. J.*, cxcvi., p. 543.

[3] *Chem. News*, xxx., p. 204. His anthracene probably was not quite pure.

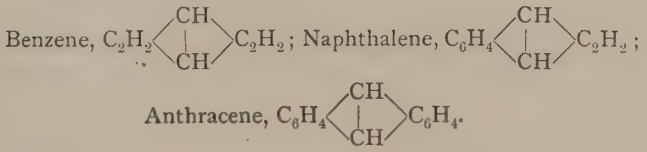
According to Bechi,[1] 100 parts of

Abs. alcohol at 16° dissolve 0·076 ; when boiling, 0·83 anthracene.
Toluene „ 16°·5 „ 0·92 ; at 100°, 12·94 „

Its solution in benzene, when exposed to sunlight, soon deposits crystals of *paranthracene* which resist the action of solvents and concentrated acids and fuse at 244°, being re-converted into anthracene. Ordinary sulphuric acid on gentle heating dissolves anthracene and becomes of a greenish colour; at a higher temperature sulphonic acids are formed. Fuming sulphuric acid acts violently upon it. Oxidizing agents convert it into anthraquinone; reducing agents into hydrocarbons richer in hydrogen; nitric acid into nitro-compounds. Dissolved in benzene, together with picric acid, it yields ruby-coloured crystals, fusing at 170° and decomposed by alcohol. With dinitroanthraquinone (Fritzsche's reagent) it gives shining, rhomboidal, purple plates: if it is not quite pure, the plates are blue; if too impure, the reaction fails altogether.[2] By the action of light it passes over into dianthracene, but this reaction is reversed by keeping the product in the dark (Luther and Weigert, *Chem. Centr.*, 1904, ii., p. 117; 1905, i., p. 1152).

Its molecular heat of combustion at constant pressure is = 1694·3 cal. (Stohmann, Kleber, and Langbein, *J. prakt. Chem.*, xl., pp. 128 and 202).

Note the natural series:—



Anthracene dihydride, $C_{14}H_{12}$.

Prepared by Graebe and Liebermann;[3] occurs in coal-tar, crystallizes in colourless plates, similar to naphthalene; fuses at 106°, begins to sublime at the same temperature, and distils at 305° without decomposition. It volatilizes with aqueous or alcoholic vapours. It has a peculiar smell, especially at a

[1] *Ber.*, 1879, p. 1978. [2] Fritzsche, *Z. für Chemie* [2], iii., p. 289.
[3] *Ber.*, 1868, p. 187.

higher temperature. It is insoluble in water, easily soluble in alcohol, ether, and benzene. In the solid state it shows no fluorescence; but its solutions have a blue fluorescence. It does not, like anthracene, yield a compound with picric acid.

Anthracene hexahydride, $C_{14}H_{16}$,

occurs together with the preceding; fuses at 63°, and boils at 290°; its physical properties, solubilities, etc., are quite similar to those of the dihydride. A tetrahydride, which was formerly assumed, does not exist.

Anthracene perhydride, $C_{14}H_{24}$.

Obtained by Lucas (*Ber.*, 1888, p. 2511) by reducing anthracene with red phosphorus and hydriodic acid at 250°. Colourless scales, melting at 88°, boiling at 270°.

Paranthracene, $C_{28}H_{20}$,

does not occur as such in coal-tar, but is formed by the action of sunlight on solutions of anthracene, from two molecules of $C_{14}H_{10}$ (Elbs[1] and Orndorf and Cameron).[2] It melts at 272° to 274°, and is thereby reconverted into anthracene.

Monomethylanthracene, $C_{15}H_{12} = C_{14}H_9 . CH_3$.

Discovered in 1874 by Weiler,[3] and since then often examined; occurs in coal-tar in small quantities.[4] It has been synthetically produced by Kraemer and Spilker, by overheating the vapours from *m*-xylene-styrolene.[5] It crystallizes from hot alcohol in thin, very bright, light yellow scales; fuses at 200° (Weiler, Fischer) or 208° to 210° (Wachendorff and Zincke); sublimes in greenish scales; boils above 360°. Insoluble in water; little soluble in alcohol, ether, and glacial acetic acid; easily soluble in chloroform, carbon disulphide, and benzene. Nitric and sulphuric acids dissolve it slowly cold, more quickly when hot. With picric acid it yields a compound similar to that obtained from anthracene. The formula given by Laurent for his "paranaphthene" was also $C_{15}H_{12}$; but he could not have had a pure compound before him.

[1] *J. prakt. Chem.*, xliv., p. 467.
[2] *Amer. Chem. J.*, xvii., p. 658.
[3] *Ber.*, 1874, p. 1185.
[4] Japp & Schultz, *ibid.*, 1877, p. 1049.
[5] *Annalen*, clxix., p. 207.

Isomethylanthracene, $C_{15}H_{12}$,

has been found by Börnstein (*Ber.*, 1906, p. 1238) in a tar obtained from a non-bituminous Westphalian coal, when distilled at the low temperature of 500° C. It melts at 202° to 204°, can be sublimed when cautiously heated, yields a red picrate, and dissolves with violet-blue fluorescence in the ordinary organic solvents.

Dimethylanthracene, $C_{16}H_{14}$,

was synthetically prepared by Van Dorp in 1872,[1] but not directly proved to exist in coal-tar. This is, however, made most probable by Kraemer and Spilker's synthesis from pseudocumenestyrolene, like its preceding homologue. It resembles the preceding, and fuses at 224° to 225°.

The methylated anthracenes cause the alizarin prepared from such material to assume a yellow tint, and thus to lose in quality.

Phenanthrene, $C_{14}H_{10}$.

This isomer of anthracene was discovered simultaneously by Graebe[2] and by Fittig and Ostermeyer.[3] It is found in the last fraction of the coal-tar oils, as a constant companion of anthracene, and forms a large portion of the crude anthracene. It is obtained from the raw material by a long series of crystallizations from alcohol, in which it is much more soluble than anthracene, and is also obtained in the factories in the purification of the latter; most easily from crude anthraquinone by extracting it with alcohol and recrystallization. It is best to remove phenols and acridine by treating the product with caustic-soda solution and sulphuric acid. Moreover, its lower boiling-point can be utilized for a preliminary separation of it from anthracene; its much lower fusing-point facilitates its identification.

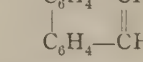
Phenanthrene, when pure, crystallizes from alcohol in colourless scales with a faint blue fluorescence. It fuses at 99° to 100°, boils at about 320° to 322° (Kraemer). Weger (*Z. angew. Chem.*, 1909, p. 342) states the fusing-point = 96°, the boiling-point = 340° (corr.). It . . . sublimes in scales less easily than anthracene. It dissolves at 13°·5 in 48 or 50

[1] *Berl. Ber.*, 1890, pp. 3169 and 3269.
[2] *Ber.*, 1873, p. 861. [3] *Annalen*, cxlvi., p. 361.

parts of alcohol (readily when hot); also in ether, benzene, glacial acetic acid, and carbon disulphide. In alcoholic solution it yields with picric acid reddish-yellow needles, fusing at 143° to 145° and soluble in hot alcohol without decomposition. Nitric acid dissolves it, forming a nitro-compound; sulphuric acid at 100° forms a sulphonic acid. Bechi (*loc. cit.*) gives its solubility as follows:—In 100 parts of

Absolute alcohol, at 16° = 2·62, at 78° = 10·8 parts.
Toluene, „ 13°·5 = 33·02, „ 100° in all proportions.

The structural formula of phenanthrene is now generally assumed to be



i.e., it is a derivative of diphenyl. This is absolutely proved by the synthesis from benzene and cumarone (Kraemer and Spilker), and from α-phenylorthodiazocinnamic acid (Pschorr).[1] It has been further studied by Rahe[2] and by Jackson and White.[3]

Graebe (*Ber.*, 1904, p. 4145) has shown that it is formed by the action of strong heat on ethyl and methylfluorene, the penta-nucleus thus passing over into the hexa-nucleus, with loss of hydrogen. A. Werner, with some of his students, has made very valuable additions to the chemistry of phenanthrene (*Annalen*, vols. 321 and 322; *Chem. Centr.*, 1902, ii., 56, 281), and so has Pschorr and his students (*Ber.*, xxxv., p. 2726; *Chem. Centr.*, 1902, ii., 642).

It was formerly regarded as a worthless substance, but seems now to take its rank among the valuable constituents of crude anthracene.

The *hydrides of phenanthrene* have been synthetically prepared, but not yet found in coal-tar (Graebe, Liebermann, and Spiegel, Bamberger, Lodter and Bretan).

Pseudophenanthrene, $C_{16}H_{12}$,

fuses at 115°; discovered by Zeidler[4] in that portion of

[1] *Ber.*, 1896, p. 496. [2] *Ibid.*, 1898, p. 1896.
[3] *Jahresb. d. Chem.*, 1880, p. 462, and 1882, p. 732.
[4] *Chem. Centr.*, 1877, p. 566.

crude anthracene which is soluble in acetic ether, together with

Synanthrene, $C_{14}H_{10}$,

fusing at 189° to 195.° Nothing accurate is known of these bodies. Synanthrene is probably identical with methylanthracene.

Fluoranthene, $C_{15}H_{10}$.

Syn. idryl. Discovered in 1877 in coal-tar by Fittig and Gebhardt.[1] It probably stands in the same relation to fluorene ($C_{13}H_{10}$) as phenanthrene ($C_{14}H_{10}$) to diphenyl ($C_{12}H_{10}$). It accompanies pyrene in the highest-boiling fractions of coal-tar, and can be separated from pyrene only by many crystallizations from alcohol, preferably those of its compound with picric acid. It crystallizes from dilute alcohol in broad, shining, large plates; from a concentrated solution, in needles. It fuses at 109°, and afterwards sublimes. It dissolves with difficulty in cold alcohol, readily in ether, chloroform, benzene, carbon disulphide, glacial acetic acid, and boiling alcohol; dissolved in concentrated sulphuric acid by gently heating, it gives it a greenish-blue, at a higher temperature a blue, and ultimately a brown colour. With nitric acid it yields a trinitro-product; with picric acid in alcoholic solution, reddish-yellow needles fusing at 183°, and decomposed on boiling with water or addition of ammonia.

Pyrene, $C_{16}H_{10}$.

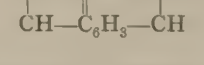
Laurent, in 1837, found pyrene in coal-tar, but probably obtained it only in a very impure state. Graebe, in 1870, prepared it pure.[2] The fractions boiling above anthracene are extracted with carbon disulphide, the filtrate is evaporated to dryness, the residue dissolved in alcohol, and a precipitate is produced by an alcoholic solution of picric acid, which is several times recrystallized from alcohol, and then decomposed by ammonia. The separated pyrene is recrystallized from alcohol. Colourless tables, fusing at 148°, subliming with difficulty, and boiling considerably above 360°. Little soluble in cold alcohol, easily in carbon disulphide, ether, benzene,

[1] *Ber.*, 1878, p. 241; *Annalen*, cxci., p. 295.
[2] *Annalen*, clviii., p. 285.

and hot alcohol. Bechi (*loc. cit.*) states that its solubility in 100 parts of

Absolute alcohol, at 16° = 1·27, at 78° = 3·08 parts.
Toluene, „ 18° = 16·54, „ 100° (very great).

It yields a nitro-product. Its picrate forms long red needles fusing at 222°, decomposed slowly by boiling water, at once by alkalis. Graebe regards it as phenylene-naphthalene, $C_{10}H_6(C_6H_4)$; it may also be represented as a diphenyl derivative in which the two nuclei are once more connected by two C_2H_2 groups,



Cf. also Bamberger and Philip (*Annalen*, ccxl., p. 147).

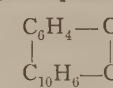
Chrysene, $C_{18}H_{12}$.

Discovered in 1817 by Robiquet and Colin when distilling amber, in 1837 by Laurent in coal-tar; afterwards investigated by many chemists. Chrysene is obtained in larger quantity only by distilling pitch down to coke, mixed with pyrene as a yellow tough mass, sometimes as a dry powder. On extracting this mass with carbon disulphide, chrysene remains behind, and is recrystallized from hot glacial acetic acid or heavy tar-oil. The latter and oil of turpentine are its best solvents; carbon disulphide dissolves only traces. Bechi states that its solubility in 100 parts of

Absolute alcohol, at 16° = 0·097, at 78° = 0·17 part.
Toluene, „ 18° = 0·24, „ 100° = 5·39 parts.

Chrysene usually forms loose, shining, yellow scales (rhombohedra with straight end face), whose colour, however, is caused by a tenaciously adhering mixture of another substance (chrysogen); in a perfectly pure state it is white. It fuses at 250°, sublimes similarly to anthracene, boils at 436°, but is at the same time partly decomposed. With picric acid and binitro-anthraquinone it forms compounds. In concentrated sulphuric acid it dissolves on being heated, with a purple colour; nitric acids yields nitro-products. It is a member of

the series, increasing by C_4H_2, to which benzene, naphthalene, phenanthrene, chrysene, and picene belong; probably it is



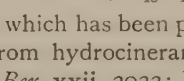
[1]

The accuracy of this formula has been proved by the syntheses of Kraemer and Spilker (*supra*), and of Bamberger and Chattaway (*Ber.*, 1893, p. 1745).

The *hydrides of chrysene*, investigated by Liebermann and Spiegel,[2] probably occur also in coal-tar.

Truxene, $C_{18}H_{12}$.

This hydrocarbon, which has been prepared from hydrindene, from dichlorindene, from hydrocineramic acid, etc., by various chemists (Hausmann, *Ber.*, xxii., 2022; Liebermann and Bergami, *ibid.*, xxii., 786; by Kipping, *ibid.*, xxvi., [2], 607; *Proc. Chem. Soc.*, Nos. 112 and 117; *J. Chem. Soc.*, lxv., pp. 276 and 495; Monthey, *Ber.*, xxxii., p. 2476) has been found in coal-tar pitch by Weger and Billmann (*Ber.*, xxxvi., 1903, p. 540), and Kraemer (*ibid.*, p 645) considers it an important constituent of the pitch. Formula:



It melts at 365° to 368° (Liebermann, *Ber.*, xxvii., p. 2417). Not soluble in all ordinary solvents; but a little in boiling xylene, chloroform, aniline, and nitrobenzene. Is but slowly acted upon by fusing potash, more so by prolonged boiling with strongest nitric acid, nitrophtalic acid and other products being formed. Treatment with the chromic acid mixture produces tribenzoylene-benzol.

Chrysogen.

Discovered in 1862 by Fritzsche[3] in coal-tar. It is the substance whose intense orange colour, even in the smallest quantity, imparts its tint to other bodies, *e.g.*, to chrysene. Its

[1] Graebe and Bungener, *Ber.*, 1879, p. 1078; Bamberger and Kranzfeld, *ibid.*, 1885, p. 1931.

[2] *Ibid.*, 1889, p. 135.

[3] *Z. für Chemie* [2], ii., p. 139.

formula is not yet established; it contains above 94 C per cent. It is isolated by repeated crystallization from light tar-oil and washing with ether and alcohol. It dissolves in 500 parts of boiling or 2500 parts of cold benzene, 2000 of boiling or 10,000 of cold glacial acetic acid. It is best obtained from boiling alcohol, in yellow scales, cohering like sal-ammoniac; the thinnest scales are pink, with gold-green lustre. Even $\frac{1}{3000}$ of it imparts to naphthalene an intense yellow colour; but its solutions are quickly bleached in the sun, star-shaped groups of colourless needles being formed. It fuses at 280° to 290°, being partly decomposed; in concentrated sulphuric acid it dissolves without change.

Retene, $C_{18}H_{18}$.

Discovered in 1837 by Fikentscher and Trommsdorff, in coal-tar by Krauss,[1] studied especially by Fritzsche[2] and by Bamberger and Hooker. Shining, unctuous scales, devoid of smell and taste, fusing at 98° to 99°, solidifying again at 90° to 95°, boiling at 350° without change, but volatilizing a little even at the ordinary temperature, strongly in the water-bath. Sinks in cold water, but floats in hot alcohol, ether, fatty and essential oils. At a red heat it yields much anthracene. It has been proved by Bamberger and Hooker[3] to be methyl-isopropyl-phenanthrene. It is most easily prepared by distilling resin-oil with sulphur (priv. comm. from J. Kraemer). Its dodecahydride has been prepared by Liebermann and Spiegel (*supra*).

Succisterene

is hardly a distinct chemical compound, but probably a mixture. Pelletier and Walter describe it as devoid of smell and taste, fusing at 160° to 162° and distilling above 300°, very little soluble in alcohol and ether. Analysis yielded 95·5 C and 5·6 H per cent.

Picene (*Parachrysene*), $C_{22}H_{14}$.

Discovered by Burg[4] in browncoal-tar, but very probably present in the heaviest coal-tar-oils; identical with Rasenack's parachrysene.[5] It is very similar to chrysene, but even less

[1] *Ann. Chem. Pharm.*, cvi., p. 391.
[2] *J. prakt. Chem.*, lxxv., p. 281.
[3] *Annalen*, ccxxix., p. 102.
[4] *Ber.*, 1880, p. 1834.
[5] *Ibid.*, 1873, p. 1041; *Wagner's Jahresber.*, 1873, p. 813.

soluble, viz., very little in boiling glacial acetic acid, benzene, and chloroform, best in coal-tar oils; boiling between 150° and 170°. Its fusing-point is higher than that of any other known hydrocarbon, viz., 337° to 339°, corrected = 345°, and it boils at 518° to 520°. It dissolves in concentrated sulphuric acid, with a green colour.

Precisely the same body was found by Graebe and Walter[1] in a product obtained by dry distillation of the purification residue of Californian petroleum. They found its formula $= C_{22}H_{14}$, which makes it a member of the series mentioned on p. 204. It fuses at 330° to 345°, and boils (as determined by Crafts's air-thermometer) at 518° to 520°. Hence also its boiling-point exceeds that of any other hydrocarbon of known formula.

Bamberger and Chattaway[2] obtained it in a purer state and found its fusing-point 364°. They proved it to be $\beta\beta$ dinaphthylene-ethylene—that is, the phenanthrene of the naphthalene series:

$$\begin{array}{l} \beta\text{—}C_{10}H_6\text{—}CH \\ \quad\quad\quad\

(*Monatsh.*, xxi., p. 118), and afterwards found in some coal-tars by Börnstein (*Ber.*, 1906, p. 1241; *cf.* also, *Chem. Centr.*, 1906, ii., 921). It fuses at 308° and sublimes when cautiously heated, over 500° C. it boils with decomposition. Very little soluble in alcohol, soluble in boiling benzene, cumene, petroleum, spirit, glacial acetic acid, chloroform, and acetone. Sulphuric acid dissolves it with dark blue colour. It is oxydized to a quinone by a solution of chromic acid in acetic acid.

Bitumens.

Badly characterized hydrocarbons, fusing with great difficulty, assumed to be present in coal-tar pitch. Carnelley[1] distinguishes two bitumens:—one boiling at 427° to 439°, which is readily soluble in benzene, and carbon disulphide, moderately in ether; and the other boiling above 439°, hardly soluble in benzene, but more easily in carbon disulphide. The latter softened at 190°, began to fuse at 220°, but was not quite liquid till it reached 330°. Both were black masses with conchoidal fracture. Evidently Carnelley himself does not assume that these two bodies were homogeneous compounds. (*Cf.* also, *supra* p. 205, what Kraemer says of truxene.)

Oxygenized Compounds.

Water, H_2O.

Methylic Alcohol, CH_4O.

Syn. wood-spirit, wood-naphtha. Boils at 63°; sp. gr. at 0° 0·818, at 20° 0·798. Occurs in wood-tar, and especially in crude wood-vinegar; not yet proved with certainty to occur in coal-tar.

Ethylic Alcohol, C_2H_6O.

Syn. spirit of wine. Boils at 78°·5; sp. gr. at 0° 0·8095, at 15°·5 0·7939. According to Witt,[2] it constitutes 2 per cent. of crude benzol; Vincent and Delachanal[3] also confirm this statement; but Kraemer[4] questions the fact, as do also K. E. Schulze (*vide supra*) and Heusler (*Ber.*, 1895, p. 488). Possibly

[1] *J. Chem. Soc.*, 1880, p. 714.
[2] *Chem. Centr.*, 1878, p. 415.
[3] *Comptes rend.*, lxxxvi., p. 340.
[4] *Chem. Ind.*, 1878, p. 126.

the mistake arose from the circumstance that the "crude benzol" of Witt and of Vincent had already been treated with sulphuric acid and caustic-soda liquor, in which case it might happen that, from the ethylene dissolved in the tar, sulphovinic acid would be formed, and decomposed by the alkaline treatment with formation of alcohol. Watson Smith also explains the formation of alcohol in this way; he could find only small traces of alcohol in London benzene.

Acetone, $C_3H_6O = CH_3 - CO - CH_3$.

Boils at 56°; sp. gr. 0·7921 at 18°. Soluble in water, alcohol, ether, etc., in all proportions. Very inflammable. Heusler has obtained it from "first runnings" of benzol by treatment with water.

Acetic Acid, $C_2H_4O_2$.

Boils at 119°; sp. gr. at 15° 1·057. Extremely important as is its occurrence in wood-tar, it seems to be nearly, if not quite, absent from coal-tar. Vincent and Delachanal (*loc. cit.*) found it on distilling crude benzol with alkali, as a product of the decomposition of methylic cyanide.

Benzoic Acid, $C_7H_6O_2$.

Melting-point 121°·4; boils at 249°·2. Found in the residues from the manufacture of phenol by K. E. Schulze (*Ber.*, 1885, p. 615). It is perhaps not present as such in the tar, but is only formed from benzonitrile during the treatment for phenols (see below under "benzonitrile").

Phenol (*Carbolic Acid*), C_6H_6O.

Syn. phenylic acid, phenylic alcohol. Discovered in 1834 by Runge,[1] more thoroughly examined by Laurent, and subsequently by many chemists. It was for a long time confused with Reichenbach's "Creosote" from beech-wood tar, in spite of Runge's and Laurent's protestations, on the authority of Reichenbach, Gmelin, and others: hence "creosote" came to be practically synonymous with "carbolic acid" (acide phénique), until all doubts were removed by Gorup-Besanez.[2]

[1] *Poggend. Ann.*, xxi., p. 69; xxxii., p. 308.

[2] *Cf.* the History of Phenol, by Schorlemmer, *J. Soc. Chem. Ind.*, 1885, p. 152.

The history, manufacture, application, and examination of carbolic acid are monographically treated by H. Koehler in his *Carbolsäure und Carbolsäurepräparate*, Berlin, 1891.

Phenol occurs very frequently in natural products of the decomposition of organic substances, especially under the influence of heat; from woody lignite, petroleum, and coals; also in various animal secretions and in the products of putrefaction. It can be artificially produced from benzene by oxidation with nascent oxygen, or even with free oxygen (Friedel and Crafts, *Bull. Soc. Chim.*, xxxi., p. 463), but commercially this is only done by the alkaline fusion of benzene-sulphonic acid. It is also obtained by the oxidation of aniline, and in many other ways.[1]

Choay (*Comptes rend.*, cxviii., p. 1211) determined the melting-point of absolutely pure phenol = 42°·5 or 43°, its boiling-point = 178°·5. It occurs much more abundantly in coal-tar than in other tars. In the pure state it forms long white needles, fusing at 42°·2 into a clear, colourless liquid, and boiling (under a pressure of 760 mm.) at 184° without decomposition. Ordinary "pure" phenol, which contains traces of cresol or water, fuses at about 35°·5 and boils at 188°. Hence the phenol examined by Adrieenz,[2] and considered exceptionally pure, which fused at 37°·8, solidified at 34°·3, and boiled at 183°·3 to 184°·1, was not absolutely pure. Really pure phenol, fusing at 42°, is less deliquescent than that melting at 35°, which contains a little cresol. In damp air phenol absorbs water, and its fusing-point is lowered by the formation of a *hydrate*, C_6H_6O, H_2O, containing 16·07 per cent. of water and fusing at 17°·2.[3] It seems to be the same as that obtained by Calvert on exposing a mixture of 4 parts of phenol with 1 part of water to a temperature of 4°, although he states its fusing-point to be 16°, and its formula $2(C_6H_6O)$, H_2O. The hydrate begins to lose water at 100°, and thus gradually arrives at the boiling-point of anhydrous phenol.

In very damp air the hydrate absorbs still more water and then remains liquid. If as much water is added to phenol as will combine with it, the resulting liquid contains about 27 per

[1] The literature on this subject is too extensive to be quoted in this place.

[2] *Ber.*, 1873, p. 443.

[3] Allen, *Analyst*, iii., p. 319.

cent. water, almost exactly corresponding to the hydrate C_6H_6O, $2H_2O$. But on shaking this liquid with 4 vols. of benzene, it gives up the whole of its phenol to the latter, the water being separated (Allen).

The specific gravity of phenol at 18° is 1·065; its expansion for the temperature t at the pressure of 760 mm. is stated by H. Kopp as follows:

$$V_t = 1 + 0{\cdot}0006744t + 0{\cdot}0000017\,21t^2 - 0{\cdot}000000000\,50408t^3.$$

Adrieenz (*loc. cit.*) gives the following table of the volumes of phenol:—

Temperature.	Spec. grav.	Volume.
Degrees.		
40	1·05433	1·01504
50	1·04663	1·02259
60	1·03804	1·03036
70	1·02890	1·04028
80	1·01950	1·04984
90	1·01015	1·05951
100	1·00116	1·06899

In spite of being deliquescent, phenol is not very easily soluble in water, but is so in all proportions in alcohol, ether, benzene, glacial acetic acid, glycerin, etc. It is usually stated that phenol dissolves in 20 parts of water; and some give even a much higher figure. Alexeieff gives the following data:—100 parts of water at 11° dissolve 4·83, at 35° 5·36, at 58° 7·33, at 77° 11·83 parts of phenol; at 84° both liquids mix in all proportions. On the other hand, 100 parts of phenol at 9° dissolve 23·3, at 32° 26·75, at 53° 31·99, at 71° 40·72 parts of water. But Allen states that liquid aqueous carbolic acid dissolves in 11·1 times its volume of cold water, corresponding to pure phenol dissolving in 10·7 times its weight of water or to the aqueous solution containing 8·56 per cent.[1] According to Hamberg,[2] pure carbolic acid (fusing-point 40° to 41°, solidifying-point 39°, boiling-point 180° to 180°·5) dissolves

[1] Other observers have found that phenol containing some water is much more soluble in an excess of water than anhydrous phenol; this perhaps explains the difference between Allen's observations and those of other chemists.

[2] *Ber.*, 1871, p. 751.

at 16° or 17° in 15 parts of water, and at 40° in 2 vols. of liquor ammoniæ of sp. gr. 0·96 (forming a clear liquid which turns milky at 17° or 18°). Other statements, attributing to it less solubility, may be explained by the presence of cresol, which lowers the solubility. The aqueous solution does not redden litmus; benzene, ether, carbon disulphide, or chloroform abstracts phenol from its aqueous solution. Cold petroleum-spirit dissolves but little of it. Schweissinger (*Pharm. Zeit.*, 1885, p. 259) gives the following particulars respecting the solubility of phenol in petroleum-spirit. One part phenol requires for its solution :—

At	43°	42°	41°	39°	37°	35°	32°	29°	27°	25°
	1	2	3	4	5	6	7	8	9	10
	23°	21°	19°	16°						
	15	20	30	40	parts of petroleum-spirit.					

The solubility in paraffin oil is about the same. This property of phenol is utilized in the manufacture of loose crystals.

Phenol has a certain affinity to bases, as manifested by their use in extracting it from tar oils, but its acid properties are only about $\frac{1}{3000}$ of those of carbonic acid (Walker, *Z. physik. Chem.*, xxxii., p. 137). Nevertheless, when brought into contact with potassium or sodium carbonate, it replaces half of the CO_2, with formation of bicarbonates, as described by Genesch in 1903 in a number of patents, to which we shall refer in Chapter IX.

The smell of carbolic acid is very similar to that of wood-tar creosote (that is, smoky), but (like the taste) it is less pronounced in very pure phenol than in impure; so that in the former it can be masked by a few drops of geranium oil, which also render it permanently liquid. The taste of phenol is both hot and sweet: it acts violently upon the epidermis, turning it white and causing it to harden or shrink. Hence it must be cautiously handled; rubbing with a fatty oil lessens the pain and the bad effects of external contact with it. Internally it acts of course as a poison, both on account of its corrosive action on the epithelium and its property of coagulating albumen; it appears to act on the nervous system by paralyzing the nerve-centres. According to Allen, even a momentary contact of strong acid with an extensive surface of

the lower parts of the body is mostly fatal, but it has comparatively little effect on the arms.

The poisonous and coagulating properties of phenol are clearly shown by its preventing the development of lower organisms, which renders it one of the most important agents for the prevention of fermentation and putrefaction, for Lister's treatment of wounds, etc.; and its technical application, apart from its employment in the manufacture of a few colouring-matters, of salicylic acid, etc., is exclusively owing to its antiseptic property.

Cf. about the poisonous action of carbolic acid, Bokorny, *Chem. Zeit.*, 1906, p. 554.

The solutions of phenol in oil do not possess the same disinfecting power as those in water (Koch, Wolffhügel, and Knorre, *J. Soc. Chem. Ind.*, 1882, p. 244).

Phenol, if not quite pure, turns red more or less quickly especially under the influence of air and light. The cause of this is not accurately known; perhaps it is owing to the formation of rosolic acid due to traces of mineral acids, in the presence of homologues and of oxygen. Frequently the reddening of phenol is attributed to traces of copper[1] or of other metals,[2] which are said to form compounds of a red colour with phenol, but not rosolic acid (Kremel). Rosolic acid is assumed to be the cause by Yvon;[3] other oxidized compounds by Ebell.[4] *Cf.* also Richardson,[5] Bach,[6] Gordon, Boes, Renter. Some ascribe the red coloration, not to impurities, but to the oxidation of phenol itself. According to Kraemer and Spilker,[7] the coloration is due to the influence of indene (p. 190).

The following reactions are characteristic for phenol:—A drop of a dilute solution of phenol gives with a solution of 1 part of molybdic acid in 10 of concentrated sulphuric acid a yellow-brown colour, soon turning purple. Heating to not above 50° assists the reaction. Since many other bodies cause the reduction of molybdic acid, this reaction is interfered with

[1] *E.g.*, Sicha, *J. Soc. Chem. Ind.*, 1882, p. 397.
[2] Kremel, *Chem. Zeit.*, 1886, Rep. 14; Meyke, *Fischer's Jahresber.*, 1883, p. 513.
[3] *Pharm. J. Trans.*, 1881, p. 1051.
[4] *Repert. anal. Chem.*, 1884, p. 17.
[5] *J. Soc. Chem. Ind.*, xii., p. 415.
[6] *Monit. Scient.* [4], viii., p. 508.
[7] *Berl. Ber.*, 1890, p. 648.

by them. By addition of ferric chloride (not in excess!) 1 part of phenol in 1000 or at most 1500 (not 3000, as usually stated) can be recognized by a purple colour; but some neutral salts interfere with this, and, on the other hand, other compounds show the same reaction. In the presence of much alcohol this reaction ceases altogether (Peters, *Z. angew. Chem.*, 1898, p. 1078). Raschig (*Z. angew. Chem.*, 1907, p. 2065) attributes this reaction to the formation of a ferri-salt of phenol, similar to the ferri-salicylate characterized by Hantzsch and Desch in 1902 (*Annalen*, cccxxiii., p. 1). Twenty c.c. of a solution of 1 part of phenol in 10,000 water, mixed with a very little liquor ammoniæ and then with a little fresh saturated chlorine-water, or, preferably, bromine-water, produce a deep indigo-blue colour. This reaction is very stable, the colour remaining unchanged for days and weeks even in the open air. On heating phenol solutions with $\frac{1}{3}$ to $\frac{1}{2}$ their bulk of a 10- or 15-per-cent. solution of mercurous nitrate, a pink colour appears, which is strongest one or two hours afterwards. This reaction is almost as sensitive as the next, and remains for some time. Even 1 part of phenol in 80,000 water can be discovered by adding fresh bromine-water, a white crystalline precipitate of tribromphenol ($C_6H_3Br_3O$) being formed, but in the case of very dilute solutions not till some time has elapsed. Uranium acetate is recommended as a test for phenols by Orlow (*Chem. Zeit. Rep.*, 1902, p. 164). According to Fiora (*Chem. Centr.*, 1901, i., p. 843) pure phenol, when treated with peppermint oil, after some time, gives a greenish-blue coloration which disappears on heating, but reappears on cooling again. Cresols, etc., do not give this reaction. Herzog (*Pharm. Zeit.*, 1907, p. 578) recommends as a reagent for phenols, diphenyl-urea-chloride, and upholds this against objections made by Raschig (*Pharm. Zeit.*, 1908).

The quantitative estimation of phenol will be described in Chapter IX., where also the commercial qualitative tests for "pure carbolic acid" will be given.

Phenol is the type of a whole class of bodies which stand as it were midway between alcohols and acids. Hence the older and industrially most usual name, "carbolic acid," is scarcely used in scientific works. The phenols form a class by themselves, viz., those aromatic compounds in which the hydrogen atoms of benzene nuclei are replaced by hydroxyl (OH). The

hydrogen of the latter is easily replaced by metals or alcoholic radicals; but the other characteristics of a real acid are absent.

Phenol is consequently more soluble even in dilute alkaline solutions than in water, with formation of easily soluble and crystallizable compounds, (*e.g.*, potash, soda, or ammonia) called carbolates or phenates (C_6H_5, ONa, etc.). These compounds are not very stable, but they are not decomposed by dilution with water. Ether and alcohol dissolve these compounds. Hence the phenols can be separated from the indifferent tar-oils by treatment with an alkali.

Concentrated sulphuric acid also dissolves phenol with formation of sulphonic acids, and thus removes it from tar-oils, which, however, easily retain a little of the sulphonic acid. Nitric acid yields nitro-products, one of which is technically important, viz., picric acid, $C_6H_2(NO_2)_3OH$. In the presence of bodies which furnish methane carbon, together with free mineral acids and oxygen, rosolic acid, $C_{19}H_{14}O_3$, is formed. Upon this is based the technical preparation of coralline from phenol, oxalic acid, and sulphuric acid—and perhaps also the reddening of impure phenol, cresol $[C_6H_4(CH_3)(OH)]$ providing the methane carbon. According to Kraemer (priv. comm.) the reddening of phenol is caused by the benzoic acid contained in crude phenol, which passes over on distillation, taking up a little iron from the still and forming therewith ferrous benzoate; this on exposure to the air is transformed into red ferric benzoate.

Cresols, $C_7H_8O = C_6H_4(CH_3)(OH)$.

Syn. oxytoluene, cresylic acid.

There are three isomers of this formula; coal-tar contains a mixture of all of these.

Orthocresol (1, 2) fuses at 30° and boils at 191° corr. (Weger); water dissolves at ordinary temperatures 2·5 vols. per cent.

Paracresol (1, 4) forms colourless prisms, fusing at 36°·5 and boiling at 202° corr. It smells like phenol, and is little soluble in water (1·8 per cent. by volume). Its aqueous solution, like that of metacresol, is coloured blue by ferric chloride.

Metacresol (1, 3) boils at 201°; it is usually obtained as a thick liquid, not solidifying at −80°; but Staedel[1] has shown that it can be obtained solid on cooling down to −18° and

[1] *Ber.*, 1885, p. 3443.

starting the crystallization by adding a crystal of phenol. The crystals melt at $+3°$ or $4°$. Water dissolves only 0·53 vol. per cent. It is asserted that metacresol is both the most efficient bactericide and yet the least poisonous of the phenols (Russig). Methods for separating the three cresols for analytical and technical purposes will be given in Chapter IX.

Commercial cresylic acid (technically sometimes styled "tricresol") is a mixture of the isomers, according to K. E. Schulze (*Ber.*, 1887, p. 410), containing 40 per cent. metacresol, 35 orthocresol, 25 paracresol (creosote from lignite-tar, according to Boyen, *Berl. Ber.*, 1893, Ref. p. 151, contains 70 per cent. metacresol, 20 to 30 paracresol, and little or no orthocresol; also some creosol, boiling over 225°); it is a colourless, refractive liquid, does not solidify at $-80°$, has a specific gravity of 1·044, is much less soluble in water and alkalis, and boils at a higher temperature than carbolic acid, about 185° to 203°. It gives the same reaction with ferric chloride as carbolic acid, and is even more strongly acted upon by strong sulphuric and nitric acids. With bromine it gives a tribromo-compound, $C_6HBr_3(CH_3)(OH)$, liquid at ordinary temperatures. Its antiseptic properties are even more strongly marked than those of carbolic acid.

Allen gives the following table showing the differences between carbolic acid (Calvert's No. 1) and cresylic acid (prepared from Calvert's No. 5 by fractionating):—

	Carbolic Acid.	Cresylic Acid.
1. Melting-point . .	Solid at ordinary temperature; liquefied by addition of water; both absolute and hydrated acid solidified by freezing-mixture.	Liquid at ordinary temperature; neither absolute nor hydrated acid is solidified by freezing-mixture.
2. Boiling-point . .	182°.	198° to 203°.
3. Solubility of hydrated acid in cold water.	1 vol. in 11 . . .	1 vol. in 29.
4. Solubility in strong solution of ammonia (sp. gr. 0·880).	Completely and readily soluble in equal volume; solution not precipitated by addition of less than 1½ volume of water.	Almost insoluble; requires 16 volumes; then forms crystalline scales.

	Carbolic Acid.	Cresylic Acid.
5. Reaction with solution of caustic soda (free from alumina) containing 6 per cent. NaOH.	Completely soluble in equal volume. Addition of the alkali solution, even up to 6 volumes, causes no change.	Insoluble in small proportions. With large excess it disappears and forms crystalline scales.
6. Reaction with solution of caustic soda containing 9 per cent. NaOH.	Completely and readily soluble in equal volume. On addition of any proportion of water up to 7 volumes the liquid remains clear, but is precipitated by 8 measures of water. Soluble in 2 measures of soda, and not precipitated by less excess than 5 or 6 measures.	Soluble in equal volume, but precipitated by adding a few drops of water, the original volume separating when water is added amounting to 1 measure. The solution in soda is re-precipitated when the alkali solution is added to the extent of 3½ measures.
7. Reaction with petroleum-spirit.	Absolute acid is miscible with hot petroleum-spirit in all proportions. Miscible with only ½ vol. of cold petroleum-spirit, precipitated by greater proportion. With 3 vols. of petroleum-spirit, bulk unchanged; upper layer contains carbolic acid, which crystallizes out on sudden cooling by freezing-mixture.	Absolute acid miscible in all proportions. No separation of crystals or liquid produced by suddenly cooling solution in 3 measures of petroleum-spirit.
8. Behaviour with glycerin of sp. gr. 1·258.	Miscible in all proportions. One measure of carbolic acid with an equal volume of glycerin is not precipitated on addition of 3 measures of water. In presence of cresylic acid less dilution is possible, 2 vols. of water being the maximum for a sample containing 25 per cent. cresylic acid.	Miscible in all proportions. One measure of cresylic acid, mixed with 1 measure of glycerin, is completely precipitated by 1 measure of water.

According to this table, cresylic acid is less soluble than carbolic acid in water, ammonia, glycerin, and caustic-soda liquor, but more easily in petroleum-spirit. Hence, though the presence of considerable quantities of cresylic acid can be discovered in carbolic acid, the utilization of the above reactions

for a quantitative estimation of these bodies is out of the question. An approximate estimation of this kind will be described later on. Water of the normal temperature dissolves 2·55 per cent. of the mixture of cresols in coal-tar.

Lunge and Zschokke[1] have made experiments on the lowering of the fusing-points of pure phenol and pure paracresol by one substance being mixed with the other in definite proportions. The results of their observations are given in the following table:—

Phenol.	Paracresol.	Fusing-point.
Per cent.	Per cent.	Degrees.
100	0	+40·5
95	5	27·8
90	10	23·9
85	15	20·3
80	20	16·7
75	25	12·6
70	30	8·6
65	35	4·7
60	40	+0·75
55	45	−2·5
50	50	−2·5
45	55	−0·9
40	60	+1·2
35	65	3·5
30	70	6·7
25	75	12·4
20	80	16·2
15	85	20·8
10	90	25·9
5	95	28·5
0	100	+32·5

Since commercial cresylic acid also contains other isomers, the foregoing table cannot be directly utilized for analytical purposes.

The *pyrocresols*, first observed by Schwarz (*Ber.*, 1882, p. 2201), bodies of the formula $C_{15}H_{14}O$, have been proved by Zmerzlikar (*Z. angew. Chem.*, 1895, p. 468) to be secondary products formed in distilling crude phenol. Bott (*J. Soc. Chem. Ind.*, 1887, p. 846) has studied them in detail.

Xylenols (*Xenols*), $C_8H_{10}O = C_6H_3(CH_3)_2OH$.

Of the six xylenols admitted by theory, four are known.

[1] *Chem. Ind.*, 1885, p. 6.

ome of these no doubt occur in coal-tar; it is also probable that the "*phlorol*" from beechwood-tar (boiling at 220°) is such a mixture.[1] The pure compounds have been obtained synthetically.

Orthoxenol (1, 2, 4) = $C_6H_3(\overset{1}{C}H_3)(\overset{2}{C}H_3)(\overset{4}{O}H)$. Fuses at 65° and boils at 222°. Crystallizes from water in long needles, from dilute alcohol in othorhombic octahedra; yields a soluble sodium salt in thin needles.

Orthoxenol (1, 2, 3) fuses at 73° and boils at 212° to 213°.

Metaxenol I. (1, 2, 3) = $C_6H_3(\overset{1}{C}H_3)(\overset{2}{O}H)(\overset{3}{C}H_3)$. Long needles or plates, fuses at 74°·5 and boils at 211° to 212° (Jacobsen), or at 73° and 216° respectively (Fittig and Hoogewerf).

Metaxenol II. (1, 3, 4) = $C_6H_3(\overset{1}{C}H_3)(\overset{3}{C}H_3)(\overset{4}{O}H)$. Colourless, strongly refractive liquid of sp. gr. 1·0362 at 0°; does not easily solidify in the cold, except when brought into contact with a crystal of the same mass (Staedel and Hoeltz, *Ber.*, 1885, p. 2921); the crystals melt at 25°. Boils at 209°, little soluble in water, miscible with alcohol and ether. Its alcoholic solution is turned green by ferric chloride, its aqueous solution blue, whilst the other xenols do not give any reaction with that salt. Found in blast-furnace tar by Watson Smith (*J. Chem. Soc.*, Jan. 1866, and priv. comm.).

Metaxenol III. (1, 3, 5) fuses at 63° and boils at 218°.

Paraxenol (1 3, 4) = $C_6H_3(\overset{1}{C}H_3)(\overset{3}{O}H)(\overset{4}{C}H_3)$. Colourless crystals, very like metaxenol I.; fuses at 75°, boils at 208° to 209°, sp. gr. at 18° = 0·9709. Solubility similar to that of the above.

There are higher phenols known, viz.:—*mesitylol*, $C_9H_{11}\cdot OH$, boiling at 220°; *pseudocumenol*, $C_9H_{11}\cdot OH$, boiling at 240°; *thymol*, $C_{10}H_{13}\cdot OH$, boiling at 230°; *carvacrol* (same formula), boiling at 233° to 235°; but their existence in coal-tar has not been proved.

Neither have the oxyphenols been proved to occur in coal-tar, whilst in wood-tar they and their ethers are the most important constituents, especially *pyrocatechol*, $C_6H_4(OH)_2$,

[1] Marasse, *Ann. Chem. Pharm.*, clii., p. 75.

homopyrocatechol, $C_6H_3(CH_3)(OH)_2$, the methylic ether of the former (*guaiacol*) and that of the latter (*creosol*).

Naphthols, $C_{10}H_8O = C_{10}H_7 \cdot OH$.

Both isomers have been found in the "green-oils" obtained in the manufacture of anthracene by K. E. Schulze (*Annalen*, ccxxvii., p. 143).

α Naphthol forms brilliant needles, belonging to the monoclinic system, smells similar to phenol, and has a burning taste. Sp. gr. 1·224. It melts at 94° to 96°, and boils at 278° to 280°. Sparingly soluble in hot water, easily in alcohol, ether, benzene, etc. Volatilizes with steam. A solution of chloride of lime with an aqueous solution of α naphthol causes a deep purple coloration and the separation of purple flakes; ferric chloride gives a white turbidity soon passing into purple.

β Naphthol forms monoclinic scales, almost devoid of smell, of a burning taste, sp. gr. 1·217; melts at 122° to 123°, boils at 294°, volatilizes very little with steam. Solubility like that of α naphthol; but chloride of lime causes only a faint yellow coloration, and ferric chloride first a greenish colour, then the separation of permanently white flakes.

Acetophenone

has been found in heavy coal-tar oils by Weissgerber (*Ber.*, 1903, 754).

Anthrol and Phenanthrol, $C_{14}H_{10}O$,

have been found, although not separated in the pure state, in the oils accompanying anthracene by Noelting (*Ber.*, 1884, p. 386) by treating the portion boiling above 300° with a solution of sodium hydrate.

Rosolic Acid, $C_{19}H_{14}O_3$.

Syn. aurin. Discovered in 1834 by Runge[1] in coal-tar; afterwards synthetically prepared simultaneously by Persoz[2] and by Kolbe and Schmitt,[3] but in a very impure state, by treating phenol with oxalic and sulphuric acids. Since then it has been

[1] *Pogg. Ann.*, xxxi., pp. 65, 512; xxxii., pp. 308, 323.
[2] Fr. P. No. 54910, of 21st July 1861.
[3] *Ann. Chem. Pharm.*, cxix., pp. 119, 169.

examined by many prominent chemists; its constitution, and even its formula, was only eventually recognized in 1878, both by E. and O. Fischer and by Graebe and Caro. The generally recognized formula for rosolic acid from phenol, which is probably the same as that contained in tar, is $C_{19}H_{14}O_3$, or, structurally,

$$\begin{matrix} C_6H_4\text{—}C\text{—}C_6H_4OH \\ \quad\quad\quad\quad\quad\quad \\ \quad\quad O\text{—}C\text{—}C_6H_4OH \end{matrix}$$

i.e., a derivative of triphenylmethane, in which three hydrogen atoms are replaced by hydroxyl, and from which one molecule of water is abstracted.[1] Hence it is formed if three phenol remainders can attach themselves to a carbon atom of the fatty series (methane carbon); and it actually forms an inner anhydride of the trioxy-triphenylmethane-carbinol. It is often assumed that its formation from phenol, oxalic acid, and sulphuric acid is due to the liberation, from the oxalic acid, of CO_2, which in the nascent state gives up its oxygen to oxidize 4H of the phenols and attaches the remainders to the vacant bonds of carbon, thus—

$$3C_6H_6O + CO_2 = C_{19}H_{14}O_2 + 2H_2O.$$

The accessory reactions which take place in the formation of corallin—*i.e.*, the crude product—cannot be noticed here. Nencki[2] and Watson Smith and Staub[3] attribute the formation of rosolic acid to the formic acid generated by the action of sulphuric acid upon phenol.

We have already (p. 215) pointed out that the conditions for the formation of rosolic acid are given when, besides phenol itself, its higher homologues containing the methyl group CH_3 are present, and if at the same time mineral acids can act upon it by separating water; but there must also be an oxidizing action: thus—

$$2C_6H_6O + C_7H_8O + 3O = C_{19}H_{14}O_3 + 3H_2O.$$

Perhaps this explains why the reddening of phenol requires the presence of air, as well as the reddening of impure

[1] Graebe and Caro proposed to keep the name *aurin* for this compound, and to apply that of *rosolic acid* to the higher homologue, made from rosaniline; but this has not been generally accepted.

Ber., 1882, p. 1578.

[3] *J. Chem. Soc.*, 1884, p. 301.

naphthalene, which in any case contains some unchanged phenol; *cf.*, however, p. 213.

In any case it must be assumed that the rosolic acid found by Runge in coal-tar was only formed by acid treatment of the products. (It has not yet been proved whether a mineral acid is absolutely necessary or not.) He obtained it by exhausting the residues from the distillation of phenol by water, dissolving in one-third of their weight of alcohol, and mixing with lime. Thus he obtained a pink solution of calcium rosolate and a brown precipitate of calcium brunolate. From the former rosolic acid is precipitated by acetic acid, and purified by repeated solution in milk of lime and percipitation by acetic acid till no more calcium brunolate separates. Finally, by dissolving in alcohol and evaporating, a hard, glassy, orange-coloured mass is obtained, whose valuable dyeing-properties were very emphatically pointed out by Runge, but were first utilized a generation afterwards.

That an oxidation process takes place in this case seems to be proved by the fact that slow heating of the heavy tar-oils with lime in the presence of air much increases the yield of rosolic acid.[1] Angus Smith went even further, by heating phenol, caustic alkali, and manganese dioxide.[2]

Brunolic Acid (?).

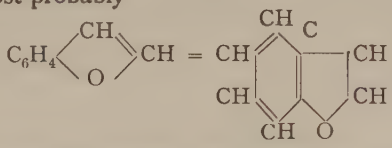
Runge thus named an acid which he isolated from the brown precipitate filtered from the solution of calcium rosolate. It was an asphalt-like, glassy mass, undoubtedly a mixture of different chemical compounds.

Cumarone, C_8H_6O.

Discovered by Kraemer and Spilker[3] in the fraction of light coal-tar oil boiling between 168° and 175°, and isolated by means of its bromine derivative. According to the Ger. P. 53792 of the Aktien-Gesellschaft für Teer- und Erdöl-Industrie, it is prepared in the pure state from these oils by precipitation with picric acid and decomposition of the picrate. Fittig and

[1] Tschelnitz, *Wiener Akad. Ber.*, xxiii., p. 169.
[2] *Chem. Gaz.*, 1858, No. 20.
[3] *Ber.*, 1890, p. 78; *Z. angew Chem.*, 1890, p. 119.

Ebert[1] prepared it synthetically, as a colourless oil, liquid at $-18°$, and boiling at 172° (corr.), spec. grav. = 1·096. Its constitution is most probably



In the presence of mineral acids cumarone is polymerized into a resinous body, *paracumarone*.[2] Cumarone has been reduced to *hydrocumarone* (Alexander, *Ber.*, 1892, p. 2409) and combined with aniline (Bizzari, *ibid.*, 1891, Ref. p. 369), the latter compound leading over to phenanthrene. This substance is also formed by passing the mixed vapours of cumarone and benzene through a red-hot iron tube :—

$$C_8H_6O + C_6H_6 = C_{14}H_{10} + H_2O.$$

Similarly naphthalene and cumarone furnish chrysene. Most probably cumarone plays an essential part in the formation of the higher hydrocarbons of coal-tar. These have been specially investigated by Stoermer (*Chem. Centr.*, 1900, ii., pp. 1071 and 1079), Stoermer and Boes (*Ber.*, 1900, p. 3013), Kraemer and Spilker (*Ber.*, 1900, p. 2257 ; 1901, p. 1887).

Paracumarone

(see above) can be directly separated from the respective tar-oils in an impure state by agitating with 10 per cent. concentrated sulphuric acid, washing the residue with water and alkali, and distilling; the paracumarone remains behind as a more or less coloured resin. It has been proposed to employ it in solution for rendering fabrics, paper, or wood impervious to water.

Methylcumarones.

Several of these have been prepared synthetically by Stoermer,[3] and they have been proved to occur in coal-tar by Stoermer and Boes (*Ber.*, 1900, p. 3013), and Boes (*Chem. Centr.*, 1901, ii., p. 1226).

The recent investigations on the cumarones and the products obtained by the decomposition of their polymers at high

[1] *Annalen*, ccxvi., p. 162. *Cf.* also Komppa, *Ber.*, 1893, p. 2969, and Dennstedt and Ahrens, *ibid.*, 1895, p. 1331.

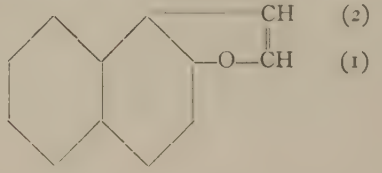
[2] *Ber.*, 1891, ref. p. 233.

[3] *Ibid.*, 1897, p. 1700.

temperatures have proved that the latter occur also in coal-tar, and have led to the conclusion that most probably coal itself contains polymeric cumarones of a complicated nature, and that the phenols of coal-tar are formed during the heating of the coal in the retort or coke-oven by the decomposition of such cumarones (Russig).

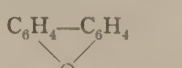
β Naphthofuran, $C_{12}H_8O$.

has been found in coal-tar by Boes (*Chem. Centr.*, 1902, i., 1356). White needles fusing at 50° to 51°, boiling at 284 to 286° C. Constitution:



Diphenylene Oxides, $C_{12}H_8O$,

obtained by Lesimple, Behr and van Dorp, Graebe, and other chemists from phenol and other materials. Afterwards discovered in coal-tar by Kraemer and Weissgerber,[1] after Kraemer and Spilker had made its presence therein probable already in 1890 (*Ber.*, 1890, p. 3281). It is found in the crude fluorene fraction of heavy coal-tar in about the same quantity at its isomers, cumarones, in the corresponding fraction of light oil, and is most easily ascertained by fusing fluorene with caustic potash which yields 12 per cent. of its derivative diphenol, $C_{12}H_{10}O_2$. Diphenylene oxide forms snow-white flakes, with a blue fluorescence, melting at 86 to 87 and boiling at 275°·5 to 276°. Its formula is:—



It is very stable against oxidizing and reducing agents, and does not take any colour in daylight. Its presence in the high-boiling fractions of coal-tar is a great impediment to the preparation of fluorene, phenanthrene, etc., in the pure state.

[1] *Ber.*, 1901, p. 1662.

The technical production of *dioxydiphenyl*, $C_{12}H_{10}O_2$, from this compound by alkaline fusion forms the subject of a patent of the Aktien Gesellschaft für Teer- und Erdöl-Industrie, Ger. P. appl. A7757.

Sulphuretted Compounds.

Hydrogen sulphide, H_2S.

Ammonium sulphide, $(NH_4)_2S$.

Ammonium sulphocyanide, $(NH_4)NCS$.

Sulphur dioxide, SO_2.

These must occur in coal-tar, as they are always present in gas-liquor (*cf.* the preceding chapter).

Carbon bisulphide, CS_2.

Boiling-point 47°. Sp. gr. 1·272. Was found in crude benzol by Vincent and Delachanal;[1] it had often been assumed to exist in tar, as it is always found in the gas. Watson Smith found 6 per cent. of CS_2 in the first runnings of rectified benzol from London gas-tar. H. L. Greville prepared it on the large scale from the calcium-sulphide purifiers of gas-works.[2]

The best reaction for carbon bisulphide is the addition of phenylhydrazine, which forms with it an insoluble compound; this will also serve for its isolation. Ahrens (*Chem. Centr.*, 1906, i., p. 510) found in the first runnings from coal-tar a sulphuretted compound similar to, but not identical with carbon bisulphide.

Carbon oxysulphide, COS,

has not yet been found in tar, but is sure to exist dissolved in it, since all conditions for its formation are present. It is a colourless gas, smelling of carbonic anhydride and slightly of hydrogen sulphide, of very faintly acid reaction. It is extremely inflammable, and with sufficient oxygen yields CO_2 and SO_2; with insufficient oxygen, or on cooling, it yields only CO_2 and S: $COS + O = CO_2 + S$.

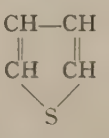
[1] *Comptes rend.*, lxxxvi., p. 340.
[2] *J. Soc. Chem. Ind.*, 1883, p. 488.

Thiophen, C_4H_4S.

This substance was discovered in commercial benzol by Victor Meyer in 1883,[1] and thoroughly examined by this chemist, his disciples, and other chemists during the following years, so that V. Meyer could as early as 1888 publish a book, *Die Thiophengruppe*, giving a synopsis of over a hundred various publications. Thiophen occurs in every variety of coal-tar benzol, up to 0·5 per cent. (also in lignite oils[2]), and is the cause of some colour-reactions previously ascribed to benzol itself by Baeyer, Classen, and Laubenheimer. It can be isolated by the peculiarity that it is more soluble in concentrated sulphuric acid than benzol. Commercial "pure" benzol is well agitated with one-tenth part concentrated sulphuric acid, the black acid-tar is separated, diluted with water and steam passed through, when crude "thiophen" (containing 30 per cent. pure thiophen) distils over.

This is dissolved in 100 parts petroleum-spirit, and the solution is agitated with one-tenth of its volume of concentrated sulphuric acid, which isolates the thiophen as a sulphonic acid. The latter is converted into a lead salt, and this is distilled with one-fourth of its weight of ammonium chloride, pure thiophen passing over.

Thiophen has also been synthetically prepared by Victor Meyer and Sandmeyer[3] from ethylene or acetylene and boiling sulphur, and by Volhard and Erdmann[4] from sodium succinate and phosphorous trisulphide; also in several other ways. Its rational formula is:—



Thiophen is a colourless mobile liquid, of a faint, not very characteristic smell. It boils at 84°; sp. gr. at 18° = 1·062. Its chemical properties are a real "mimicry" of those of benzene. It is insoluble in water, miscible in all proportions with benzene and petroleum-spirit, soluble in concentrated sulphuric acid with dark brown colour. Alkalis do not change

[1] *Berl. Ber.*, xvi., p. 1465.
[2] *Ibid.*, xvi., p. 2176.
[3] *Ibid.*, xxviii., p. 493.
[4] *Ber.*, xviii., p. 454.

it; nitric acid acts violently upon it, and forms a nitro-compound which is easily reduced to an amide-compound. It gives several colour-reactions; one of the best is the blue colour produced by nitrosulphuric acid.[1]

The methods for estimating and removing thiophen will be described later on.

Methylthiophen (*Thiotolen*), C_5H_6S,

discovered by V. Meyer and Kreis [2] in commercial toluol. There are two isomers:

α Thiotolen boils at 112° to 113°.

β Thiotolen also boils at 113°; sp. gr. of the mixture at 18° = 1·019. These two modifications are distinguished by yielding different products on oxidation with potassium permanganate. Both can be also synthetically prepared.

Dimethylthiophens (*Thioxens*), C_6H_8S.

The mixture of these thioxens was first isolated from commercial xylol by K. E. Schulze.[3] Four isomers are possible, and all of them have been synthetically produced. They boil between 135° and 138°.

Tri- and tetramethylthiophens have been produced by synthesis, but have not yet been proved to exist in tar-oils. The same is also true of *biophen*,[4] $C_4H_4S_2$; *dithienyl*,[5] $C_8H_6S_2$; *trithienyl*,[6] $C_{12}H_8S_3$; *thionaphthene*,[7] C_8H_6S; and *thiophtene*,[8] $C_6H_4S_2$.

Diphenylene sulphide, $C_{12}H_8S$,

is indicated by Kraemer and Weissgerber (*Ber.*, 1901, 1662), as occurring in the high-boiling fractions of coal-tar, together with the analogous oxide (p. 224), but it has not been isolated in the pure state. It seems to be the cause of the reddening of crude fluorene and phenanthrene when exposed to sunlight.

[1] Liebermann, *Ber.*, 1887, p. 3231.
[2] *Berl. Ber.*, xvi., pp. 1624, 2970; xvii., p. 787.
[3] *Ibid.*, xvii., p. 2852. [4] Levy, *J. Chem Soc.*, lxii., p. 216.
[5] Schmidt and Schulz, *Ber.*, xvii., p. 789.
[6] Renard, *Comptes rend.*, cxii., p. 79.
[7] Gattermann and Lockhart, *Ber.*, xxvii., p. 2808.
[8] Biedermann and Jacobson, *ibid.*, xix., p. 2444.

Mercaptans,

or similar sulphuretted compounds having a disagreeable smell, are probably present in coal-tar. The alliol of which Mansfield stated the boiling-point to be 70° to 80°, and of which he obtained 30 to 40 g. from 50 litres of tar, is perhaps a mixture of such compounds, although carbon bisulphide might be also included. Vohl has found, in crude benzene, sulphuretted bodies boiling below 80°.

				Sp. gr.
Methyl mercaptan,	$CH_3 . SH$,	boils at	20°	
Methylic sulphide,	$(CH_3)_2S$,	„	41°	0·845
Ethyl mercaptan,	$C_2H_5 . SH$,	„	36°	0·831
Ethylic sulphide,	$(C_2H_5)_2S$,	„	91°	0·852
Etc.				

Free Sulphur

has been found by Kehlstadt[1] in the distillates of coal-tar. It is probably formed from SO_2 and H_2S under the action of water.

Nitrogenized Compounds.

A. Basic.

Ammonia, NH_3,

has been already mentioned as ammonium sulphide and sulphocyanide. It occurs also as carbonate, and forms the most important constituent of gas-liquor. A colourless gas, of the well-known pungent smell, sp. gr. 0·5888, condenses at −40° to a liquid, and solidifies at −70°. Its ready solubility in water, the strongly basic properties of this solution, etc., are universally known.

Substituted Ammonias

of the fatty series probably occur in gas-liquor, and consequently in tar. We shall only quote the boiling-points, etc., of the lowest members.

Methylamine, $NH_2(CH_3)$, is a gas. One vol. water at 12° absorbs 1040 vols. of it. It is inflammable, and smells both of fish and ammonia.

[1] *Ber.*, 1880, p. 1345.

Dimethylamine, $NH(CH_3)_2$, boils at 8° to 9° ; readily soluble in water. Smell strongly ammoniacal.

Trimethylamine, $N(CH_3)_3$, boils at 9°·3 ; readily soluble in water. Smells of ammonia and herring-brine, in which it occurs abundantly.

Ethylamine, $NH_2(C_2H_5)$, boils at 18°·7 ; readily soluble.

Diethylamine, $NH(C_2H_5)_2$, boils at 57°·5 ; readily soluble.

Triethylamine $N(C_2H_5)_3$, boils at 91° ; little soluble.

The higher members and the extremely numerous mixed amines cannot be noticed here.

Cespitine, $C_5H_{13}N$,

is a base of unknown constitution, isomeric with amylamine and boiling at the same temperature (95°). It was discovered by Church and Owen. A colourless oil of strong smell, but not so disagreeable as that of amylamine ; readily soluble in water, but not in concentrated solution of caustic soda. Lighter than water, Church and Owen suppose it to contain a trivalent radical $(C_5H_{13})'''$. Fritzsche thought he had found it in coal-tar, but Goldschmidt and Constam consider Fritzsche's cespitine to be their pyridine hydrate (see below).

Aniline, $C_6H_5 . NH_2$.

Syn. phenylamine, amidobenzene, etc. Discovered in 1826 by Unverdorben in coal-tar, in 1834 by Runge (who called it kyanol). A colourless liquid, rapidly turning yellow, then red or brown, of a peculiar faint smell and burning taste. Solidifies at −8° (some say, not even at −20°) and boils at 182° ; the vapour burns readily. Sp. gr. at 16° = 1·020. It possesses poisonous properties, especially for smaller animals. Water dissolves about 2 per cent. ; and aniline dissolves some water itself. Readily soluble in alcohol, ether, acetone, carbon, bisulphide, hydrocarbons, etc. It dissolves sulphur, phosphorus, camphor, rosin. The aqueous solution has only faintly basic properties, and does not even turn red litmus blue ; but at a higher temperature it expels ammonia from its salts, whilst in the cold it is precipitated by ammonia. With chloride of lime it turns purple (this has been explained by Raschig, *Z. angew. Chem.*, 1907, p. 2071, by the formation of an indophenol) ; with potassium bichromate, blue. Its aqueous solutions precipitate

the oxides from the salts of iron, zinc, and aluminium. With the mineral acids it forms salts which are readily soluble in water and alcohol and readily crystallize; they are white when quite pure, but redden quickly in the air and acquire a faint smell.

Immense as is the importance of the aniline made from coal-tar benzol, its direct occurrence in coal-tar is yet of small moment. In that substance it is practically only an impurity, from which the hydrocarbons must be freed by acid treatment; neither does it seem feasible to extract at a profit the small quantity present in coal-tar.

Probably the basic body which former inquirers extracted from coal-tar, and which yielded the characteristic reactions of aniline, contained only a small percentage of real aniline.

According to Watson Smith,[1] aniline occurs in all distillates of coal-tar, principally (as might be expected from its boiling-point) in the light oils of sp. gr. 0·900 to 1·000. Eugen Oehler (*Z. angew. Chem.*, 1899, p. 561) found it also in browncoal tar-oils.

The *homologues of aniline* (*toluidine*, etc.) have not yet been found in coal-tar, but it is most likely that they are contained in it.

Pyridine Series.

This series includes a number of bases of the formula $C_nH_{2n-5}N$, from pyridine to viridine. They are characterized by the "pyridine nucleus," which is quite analogous to the benzene nucleus, but contains N in lieu of one atom of C. They are very stable, even towards oxidizing agents. They occur chiefly in the tar-oils of sp. gr. 0·900 to 0·990.

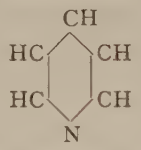
The pyridine bases found in coal-tar have been reinvestigated by A. W. Hofmann (*Ber.*, 1881, p. 1497), and by Goldschmidt and Constam (*ibid.*, 1883, p. 2976). This and the quinoline series are of very great importance, since it has been proved that the natural alkaloids are derivatives of pyridine, and some compounds, very useful for medical purposes (*e.g.*, antipyrine), have been synthetically produced from them.

Pyridine, C_5H_5N.

Discovered by Anderson in bone-tar, by Greville Williams

[1] *J. Chem. Soc.*, 1874, p. 853.

in coal-tar. Häussermann (private communication) found as much as 0·1 per cent. in commercial 50-per-cent. benzol, and 0·25 per cent. in the toluol made from this. Ahrens and Dennstedt[1] found it in coal-gas, Rosenthal in oil from lignite,[2] Loofl[3] in wood-tar, etc., etc. Its synthesis has not yet been effected with much success; but Dennstedt and Zimmermann[4] have obtained it from pyrrol. Its structural formula is



and it presents very great interest as the starting-point for a long series of important derivatives.

Pyridine is a colourless, mobile liquid of penetrating smell. Sp. gr. at 0° = 0·9858; boils at 116°·7 (Anderson) or 115° (Thenius). Miscible with water in all proportions, and reprecipitated by caustic potash or soda. Turns red litmus blue, gives off white vapours with hydrochloric acid, precipitates the salts of zinc, iron, manganese, and aluminium. Resists the action of fuming nitric and chromic acids. With the acids it forms stable salts readily soluble in water and alcohol, which can be dried at 100°, and hardly turn brown in the air. Vongerichten (*Ber.*, 1899, p. 2571) has described a reaction on pyridine by *α* dinitrochlorbenzene. Helch (*Chem. Centr.*, 1902, ii., 146) describes some reactions for distinguishing pyridine from other bases. Braeutigam (*Chem. Centr.*, 1902, ii., 466) states that by a solution of tannic acid in 25 parts of water very little pyridine (1 : 6000) can be proved by the formation of a precipitate.

Pyridine, in a solution of 1 : 700, coagulates albumina, and is therefore a strong bactericidal agent. It is recommended as a healing agent for the stings of hornets, and even as a remedy against the tendency to drink!

Pyridine, according to Bedson (*J. Soc. Chem. Ind.*, 1908, p. 147) and Donath (*Z. angew. Chem.*, 1906, p. 657) has a solvent action on the "bituminous" constituents of coal-tars, leaving a

[1] *Ber.*, 1894, p. 601.
[2] *Chem. Zeit.*, 1890, p. 873.
[3] *Ber.*, 1893, Ref. p. 710.
[4] *Ibid.*, 1885, p. 3317.

residue of almost coke-like character. This property may possibly be turned to important technical purposes if a proper use is found for the substances thus extracted from coal, for instance for the purification of anthracene.

The physico-chemical properties of mixtures of pyridine and water have been thoroughly examined by Hartley, Thomas, and Applebey (*J. Chem. Soc.*, 1908, xciii., pp. 538, 561).

Goldschmidt and Constam found in coal-tar a molecular compound of pyridine and water, C_5H_5N, $3H_2O$, of sp. gr. 1·0219, boiling at 92° to 93°, and smelling like pyridine.

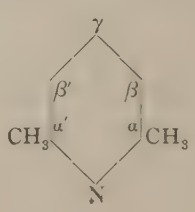
Picoline, $C_6H_7N = C_5H_4 . CH_3 . N$.

Syn. odorine. Isomeric with aniline. Discovered by Unverdorben in bone-oil, by Anderson in coal-tar. A colourless, mobile liquid of penetrating smell. Boils at 135°; sp. gr. at 0° = 0·9613 (Anderson), at 22° = 0·933 (Thenius). Its solubility, salts, and basic properties resemble those of pyridine. Coal-tar picoline is no doubt α picoline, viz., orthomethyl-pyridine (Goldschmidt and Constam); but γ pyridine is present in small quantities (K. E. Schulze, *Ber.*, 1887, p. 413), and Mohler (*ibid.*, 1893, p. 1414) proved also the presence of β picoline. γ picoline has also been isolated from these oils by Ahrens (*Ber.*, 1905, p. 155).

Lutidines, C_7H_9N.

The first lutidine was found in tar-oils by Anderson in 1851, and other bases of the same composition were discovered in different materials by Greville Williams, Church and Owen, and Thenius. Much later it was proved that these bases are mixtures of isomers, of which 6 dimethyl-pyridines and 3 ethyl-pyridines are possible, and mostly also known.

$\alpha\alpha'$ lutidine,



has been isolated from coal-tar oils by Lunge and Rosenberg,[1] also by K. E. Schulze and others.

α γ lutidine has been isolated by the same. Smells like cucumber; boils at 156° to 157°.

α β lutidine has been found by Ahrens (*Chem. Centr.*, 1906, i., p. 510) in the commercial "α β Picoline" sold by the Erkner works. It boils at 162° to 163°; its picrate melts at 183°, and is almost insoluble in alcohol.

α β′ lutidine has been proved in coal-tar oils, in the fraction boiling between 150° to 170°, by Lunge and Rosenberg.

β γ lutidine was isolated from coal-tar by Ahrens;[2] boils at 163°·5 to 164°·5.

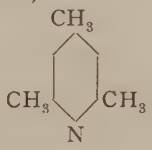
β β′ lutidine has been only synthetically produced; boils at 169° to 170°.

The 3 ethyl-pyridines have been obtained by synthesis; their presence in coal-tar is not probable. Boiling-point 164° to 166°.

Collidines, $C_8H_{11}N$.

Twenty-two isomers are possible, of which only a few have been proved in coal-tar.

The *symmetrical collidine*,



was found by Lunge and Mohler[3] in coal-tar, after having been previously synthetically prepared by Kraemer (*Ber.*, 1870, p. 262) from ethylidene bichloride and ammonia.

α′ β γ trymethyl-pyridine was found in coal-tar, with the former, by Ahrens.[4] Boils at 165° to 168°.

Parvolines, $C_9H_{13}N$.

Six of the 54 possible isomers are known; in coal-tar only tetramethylpyridines seem to be present.[5] The parvoline boiling at 188°, said by Thenius to occur in coal-tar, was not

[1] *Berl. Ber.*, 1887, p. 409.
[2] *Ibid.*, 1896, p. 2999.
[3] *Ber.*, 1888, p. 1006.
[4] *Ibid.*, 1896, p. 2999.
[5] Dürkopf and Göttich, *ibid.*, 1890, p. 1110.

found by Ahrens,[1] but he obtained another, boiling at 232° to 234°.

Coridines, $C_{10}H_{15}N$.

That indicated by Thenius, boiling at 211°, was not found by Ahrens; the base obtained by Thenius was probably a mixture. A similar base has been found by Zaloziecki[2] in Galician petroleum.

Rubidine, $C_{11}H_{17}N$.

Discovered by Thenius. A colourless oil of faint smell, boils at 230°, turns viscid at −17°, insoluble in water, soluble in alcohol, ether, etc. Sp. gr. at 22° = 1·017. It precipitates some oxides from their salts. Its salts do not crystallize well, and turn pink in the air; chloride of lime turns it pink; it stains pine-wood moistened with hydrochloric acid a red colour.

Viridine, $C_{12}H_{19}N$.

Discovered by Thenius. A yellowish oil, of sweet aromatic smell; boils at 251°, and is not solidified at −17°. Does not colour in the air; very little soluble in water. Sp. gr. at 22° = 1·024.

Neither rubidine nor viridine has been found by Ahrens in coal-tar, and their existence cannot be considered proved.

Quinoline Series.

Quinoline contains a benzene nucleus attached to a pyridine nucleus. It was first investigated by Greville Williams,[3] and has recently become of much more importance, since some of its members have been synthetically prepared and have found practical application.

The theoretical study of quinoline has been principally advanced by Körner;[4] its synthesis was first effected by Skraup[5] from glycerine, nitrobenzene, and sulphuric acid, and subsequently in many other ways.

Quinoline or Leucoline, C_9H_7N.

Discovered in 1834 by Runge. It was assumed for a long time that the "leucoline" found in coal-tar was not the same as,

[1] Dürkopf and Göttich, *ibid.*, 1895, p. 795.
[2] *Ber.*, 1892, iii., p. 732.
[3] *J. Chem. Soc.* [2], i., p. 375.
[4] *Gazz. Chim.*, xi., p. 548.
[5] *Monatsh.*, i., p. 317; ii., p. 141.

but only isomeric with, the "quinoline" obtained from cinchonine; but it was shown by Hoogewerf and van Dorp[1] that they are identical. It boils at 239° to 240°, and has a specific gravity of 1·081, a penetrating smell, and burning taste. It is little soluble in water, readily in alcohol and ether. With potassium-mercuric iodide it yields, even in very dilute solutions, a yellowish-white precipitate, which on addition of hydrochloric acid turns into amber-coloured needles. Found by Doebner[2] also in lignite oils and synthetically produced by Baeyer.[3]

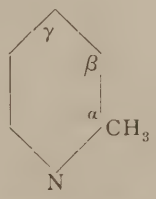
Isoquinoline, C_9H_7N.

Found by Hoogewerf and van Dorp together with the preceding; boils at 236° to 237°; fuses at 18° to 23°.

Methylquinolines (*Quinaldines*), $C_{10}H_9N$.

Of the nine possible isomers, most have been synthetically produced. The following have been proved to exist in coal-tar:—

α *methylquinoline* (*quinaldine*),



forms, according to E. Jacobsen and Reimer,[4] 25 per cent. of commercial coal-tar quinoline; synthetically produced by Doebner and v. Miller.[5] Colourless liquid, strongly refractive, boils at 238° to 239°.

γ *methylquinoline* (*lepidine*), first obtained by Greville Williams from cinchonine. Smells like quinoline, boils at 256° to 258°. Probably identical with the *iridoline* found by Greville Williams[6] in coal-tar, and stated to boil between 252° and 257°; sp. gr. at 15° = 1·072.

[1] *Berl. Ber.*, 1883, p. 425.
[2] *Ibid.*, 1895, p. 106.
[3] *Ibid.*, xii., p. 1320.
[4] *Ber.*, 1883, p. 1082.
[5] *Ibid.*, 1881, p. 2812.
[6] *Jahresber.*, 1855, p. 550.

Dimethylquinolines, $(CH_3)_2C_9H_5N$.

One of these has been found in coal-tar by Greville Williams and described as *cryptidine*, boiling at 274°; it is probably identical with the 2, 3 or 3, 4 dimethylquinoline of Berend.[1]

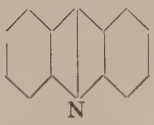
Acridine, $C_{13}H_9N$.

Discovered by Graebe and Caro[2] in crude anthracene; re-investigated by Riedel[3] and Bernthsen and Bender.[4] Obtained by extracting crude anthracene with dilute sulphuric acid, precipitating by potassium chromate, purifying the chromate by recrystallization, precipitating the base by ammonia, and recrystallizing the same from hot water. Or the hydrochlorate is recrystallized and decomposed by ammonia. Acridine crystallizes in orthorhombic prisms, which are colourless if very small, brown if rather large. It fuses at 111°, distils above 360° without change, sublimes at 100°, and is carried over by aqueous vapour. It is sparingly soluble in cold, more soluble in hot water, and readily so in ether, alcohol, carbon bisulphide, and hydrocarbons. It possesses a faint alkaline reaction; but even very dilute solutions of its salts cause acute stinging when applied to the skin; its dust in very minute quantity causes most violent sneezing. (This property of acridine is sometimes very inconvenient to the workmen in subliming crude anthracene, especially in summer-time, when they have to protect the skin of the face by rubbing fat upon it.) It has a strong destroying action on infusoria, especially in sunlight (Raab, *Chem. Centr.*, 1900, i., pp. 491, 1135). Sulphuric acid attacks acridine only at 200; hydrochloric acid and caustic potash do not attack it even at 280°; while zinc-dust, soda-lime, and many oxidizing agents do not act upon it at all. Nitric acid forms nitro-compounds. With the acids it forms salts of a yellow colour, easily soluble and crystallizable; their dilute solutions fluoresce strongly with a blue colour, more concentrated ones green, but very concentrated solutions do not show any fluorescence.

Acridine has been synthetically produced by Bernthsen[5] and

[1] *Ber.*, xvii., pp. 1489, 2716.
[2] *Ibid.*, 1872, p. 15.
[3] *Ibid.*, 1883, p. 1611.
[4] *Ibid.*, p. 1802.
[5] *Ibid.*, xvi., p. 1808.

E. Fischer;[1] *cf.* Riedel.[2] Graebe proved its structural formula to be:



Methylacridines have as yet only been obtained by synthesis; *cf.* Bernthsen and Bender[3] and Graebe.[4]

The *hydrides* of acridine have been found in coal-tar by Kraemer and Spilker (*Ber.*, 1896, p. 561), methylacridine hydride by Boes, who (*Chem. Zeit. Rep.*, 1902, p. 308) has also found hydroacridine in anthracene oil, by extracting it with sulphuric acid and precipitating with water or extracting with ether. This compound has no basic properties.

Other Bases.

G. C. Robinson and W. L. Goodwin have obtained the following bases from the "vitriol-tar" of Scotch shale-oil:—[5]

Tetracoline,	$C_{12}H_{13}N$,	boiling at	290° to 295°
Pentacoline,	$C_{13}H_{15}N$,	„	305° „ 310°
Hexacoline,	$C_{14}H_{17}N$,	„	325° „ 330°
Heptacoline,	$C_{15}H_{19}N$,	„	345° „ 350°
Octacoline,	$C_{16}H_{21}N$,	„	360° „ 365°

Probably other bases of still higher boiling-points are also present in that tar.

B. Not Basic.

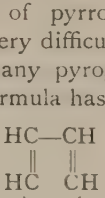
Pyrrol, C_4H_5N.

Discovered in coal-tar by Runge, isolated in the pure state from bone-oil by Anderson. Prepared by distilling the basic oils after saturation with sulphuric acid, and fractionating. A colourless liquid of chloroform-like smell and burning taste; boils at 133°; sp. gr. 1·077. Little soluble in water, insoluble in alkalis, readily soluble in ether and alcohol, slowly in dilute acids. In the air it turns brown, but is again rendered colour-

[1] *Ber.*, xvi., p. 1820; xvii., p. 101.
[2] *Ibid.*, xvi., p. 1609.
[3] *Ibid.*, xvi., p. 1808.
[4] *Ibid.*, 1894, p. 641.
[5] *Transact. Royal Soc. Edin.*, 1878, p. 561, and 1879, p. 265.

less by distillation. It tinges a piece of resinous fir-wood moistened with hydrochloric acid, first pink, then crimson. It is indifferent towards most reagents, but is perhaps very slightly basic. No salts of it are known. With potash it forms a compound not decomposable by heat, but at once decomposed by water. The quantity of pyrrol present in coal-tar is extremely small, and it is very difficult of extraction.

Pyrrol is formed in many pyrogenetic reactions, also by synthesis. Its structural formula has been proved by Baeyer:



This shows its analogy to furane and thiophen, and it really exhibits colour-reactions similar to the latter (V. Meyer[1]).

Methyl Pyrrols

have been synthetically produced; found also in bone-oil by Anderson, by Ciamician and Weidel,[2] and by Dennstedt and Lehne,[3] but not yet obtained from coal-tar.

Cyanogen Compounds.

We have already mentioned ammonium sulphocyanide. According to Vincent and Delachanal,[4] tar contains also *methylic cyanide* (aceto-nitrile), $CH_3-C\equiv N$, which under the action of alkalis takes up the elements of water and yields acetic acid and ammonia. They found it in Paris benzol, together with carbon bisulphide, in that fraction of benzol which boils below 80°. This has been confirmed by Heusler (*Ber.*, 1885, p. 615).

Methylic cyanide boils at 77°; sp. gr. 0·835. A colourless liquid of peculiar, not disagreeable smell, miscible with water in all proportions, and burning with a purple-bordered flame.

Similar compounds have been found in light coal-tar oils by Noelting,[5] who considers them to be either methyl-isocyanide, boiling at 59·6, or ethyl-isocyanide, boiling at 78°·1, and

[1] *Ber.*, xvi., p. 2974.
[2] *Ibid.*, xiii., p. 77.
[3] *Ibid.*, 1889, pp. 1918, 1920, 1924.
[4] *Comptes rend.*, lxxxvi., p. 340.
[5] *Bull. Soc. Ind. Mulhouse*, 1884, p. 461.

ascribes to them the poisonous action sometimes noticed with such light oils.

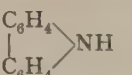
Benzonitrile, C_6H_5, CN, has not been directly obtained from coal-tar, but is evidently the source of the benzoic acid found by K. E. Schulze in the residues from the manufacture of carbolic acid. It must be present in coal-tar in somewhat considerable quantities, as the manufacture of benzoic acid, derived from that nitrile, has been patented by the Aktien-Gesellschaft für Teer- und Erdöl-Industrie (Ger. P. 109122; Fr. P. 287934); *cf.* Chapter IX.

Carbazol, $C_{12}H_9N$.

Syn. imidodiphenyl. Discovered by Graebe and Glaser[1] in the residue from the purification of anthracene by caustic potash (Chapter VII.), in which a combination of it with potash, decomposable by water, is contained. It is always an important constituent of crude anthracene. Its properties are very similar to those of a hydrocarbon; like the hydrocarbons, it forms a compound with picric acid, fusing at 182° in large red prisms, which may be employed for preparing pure carbazol. The latter can also be purified by recrystallizing or subliming. It forms white scales or plates, insoluble in water, sparingly soluble in cold alcohol, ether, benzene, chloroform, more so at a higher temperature, and very soluble in pyridine; 100 parts of toluene dissolve at 16°·5 0·55, at 100° 5·46 parts; 100 parts absolute alcohol at 14° 0·92, at 78° 3·88 parts. Fusing-point 238°; it sublimes readily and boils near 355°. It dissolves in pure cold sulphuric acid, the solution having a yellow colour; the most minute traces of nitric acid, chromic acid, chlorine, or other oxidizing agents produce an intense green colour. The chief characteristic reactions are: the red colour produced by HCl vapours on a firwood-splinter, soaked with the alcoholic solution of carbazol; the blue colour produced with isatin and sulphuric acid; and the crimson colour produced with a mixture of benzoic, acetic, and sulphuric acid. Water precipitates it unchanged from the cold solution in sulphuric acid; by heating, a sulphonic acid is formed. Nitric acid yields nitro-products. Carbazol is not changed by igniting with soda-lime, caustic lime, zinc-dust, etc.; on igniting with potash-lime a portion is decomposed, ammonia

[1] *Ann. Chem. Pharm.*, clxiii., p. 343; clxx., p. 88.

being formed. It has no basic properties, and forms no salts with acids, but a compound with acetyl and with potassium, in which the hydrogen of the imido-group is replaced by acetyl or potassium. It is the imido-compound of diphenyl:



as proved by its synthesis. Several homologues and substituted carbazols have been synthetically produced.

A quantitative estimation of carbazol, according to Vaubel (*Z. angew. Chem.*, 1901, p. 784), can be made by titrating it in a solution in glacial acetic acid by means of bromine, each molecule of carbazol taking up 2 molecules of bromine.

Phenylnaphthyl-carbazol, $C_{16}H_{11}N$.

Syn. imidophenylnaphthyl. Discovered by Brunck, examined by Graebe and Knecht[1] (who obtained it also synthetically). Is obtained by subliming the residue from distilling crude anthracene. Intensely yellow, but only by the admixture of some unknown substance; for on being fused with potassium hydrate it turns white. Almost insoluble in cold, very little soluble in boiling benzene or glacial acetic acid, more soluble in hot aniline. Toluene and absolute alcohol, when cold, dissolve next to nothing of it; boiling toluene dissolves 0·39 to 0·57, alcohol 0·25 per cent. The solutions have an intense blue fluorescence. It fuses at 330°, and has a higher boiling-point than sulphur. Its behaviour to sulphuric acid, etc., resembles that of carbazol.

Free Carbon (so-called)

is found in every description of coal-tar, partly owing to coal-dust or coke-dust being mechanically carried out of the retort, but mostly by decomposition of vapours on the hot sides of the retort, as proved by Köhler.[2] Coke-tar contains much less free carbon than gas-tar (Kraemer, *J. Gasbeleucht.*, 1887). Speculations on the formation of free carbon in tar have been made by Bone and Jordan (*Chem. Zeit.*, 1901, p. 591). It is

[1] *Ber.*, 1879, pp. 341, 2241. [2] *Z. angew. Chem.*, 1888, p. 577.

mostly estimated by treating the tar with indifferent solvents. especially hot benzene, till nothing further is dissolved. The carbon found in German coal-tar by this method varies from 7 to 33 per cent.; tar containing much of it is not very saleable, owing to the difficulty of distilling it down to hard pitch without injuring the stills. It is, however, certain that washing the tar or pitch with benzene, etc., does not yield really pure carbon, but only substances similar to anthracite or coke. Donath and Asriel (*Chem. Centr.*, 1903, i., p. 1099) found in so-called free carbon 2·3 per cent. H., 3·7 N, 7·13 O, and only 89·2 per cent. real carbon.

Hadwick (*Oest. Chem. Zeit.*, vii., p. 365), found in Westphalian coke-tar on the average 4 per cent., but sometimes as little as 0·5 per cent. "free carbon," in gas-tar 20 to 25 per cent. His method for estimating the free carbon, to which we shall refer in a following chapter, yields less than that mentioned above, and always yields a smaller percentage, but probably correctly so.

We come back to "free carbon" in Chapters V. and VI.

Theory of the Formation of the Constituents of Coal-tar.[1]

The fact that coal-tar contains principally aromatic substances was long ago explained by the assumption that coal is a mixture of compounds of the aromatic series, especially since Guimet had proved the non-existence of free carbon in tar. Baltzer (*Vierteljahrschr. d. Zürcher naturf. Ges.*, 1873) even went so far as to give hypothetical formulæ for various descriptions of coal. This, of course, only shows that coal may contain complicated compounds, from which the constituents of tar are formed by splitting-up.

Berthelot has, in a number of papers published in the *Ann. Chim. Phys.* in 1866, 1867, 1869, and 1877, formulated a complete theory of the building-up and the splitting-up of compounds by pyrogenetic reactions. Complex compounds are formed, which are decomposed into simpler ones, and these unite again to form higher compounds, thus producing a very complicated equilibrium among a large number of hydro-

[1] *Cf.* also the theory of Mills, *supra* p. 6, which is very adversely criticised by Dittmar, *Chem. Ind.*, 1891, p. 512.

carbons. Hydrogen largely enters into this series of reactions, both by being split off and by being added to other compounds.

Acetylene seems to play a very important part in the formation of the substances composing coal-tar. According to Berthelot,[1] on heating acetylene over mercury in a bent glass tube up to the softening-point (*i.e.*, to a dark red) there was produced, together with a number of secondary products occurring in small quantity, a large amount of benzene, styrolene, naphthalene, retene, etc. At a bright red heat another kind of decomposition set in; then acetylene was almost completely split up into its elements. Berthelot consequently regards benzene as triacetylene, styrolene as tetracetylene, retene as enneacetylene: thus,

$$3C_2H_2 = C_6H_6, \quad \text{benzene}$$
$$4C_2H_2 = C_8H_8, \quad \text{styrolene}$$
$$9C_2H_2 = C_{18}H_{18}, \quad \text{retene, etc.}$$

The fatty bodies likewise yield acetylene under the action of heat; and Berthelot ascribes the formation of aromatic compounds, always observed in this case, to the secondary condensation of acetylene by itself and with other compounds.

Similar conclusions are arrived at by O. Jacobsen,[2] who, besides acetylene, assumes its next homologue, allylene, C_3H_4, to participate in the synthesis. This is shown by these equations:

$$3C_2H_2 = C_6H_6, \quad \text{benzene}$$
$$2C_2H_2 + C_3H_4 = C_7H_8, \quad \text{toluene}$$
$$C_2H_2 + 2C_3H_4 = C_8H_{10}, \quad \text{xylenes (three)}$$
$$3C_3H_4 = C_9H_{12}, \quad \text{mesitylene and pseudocumene.}$$

This hypothesis would explain why,

1st, besides benzene, only those homologues occur the lateral chains of which consist of methyl;[3]

[1] *Comptes rend.*, lxii., pp. 905, 947. [2] *Ber.*, 1877, p. 853.

[3] Jacobsen himself has had to modify this part of his theory. In the *Ber.*, 1886, p. 2515, he declares it to be proved that coal-tar contains benzene substitution-products with longer lateral chains, but he was not able to obtain these in sufficient quantity to identify them.

2nd, the methylbenzenes found in tar-oil do not extend beyond the tri-derivatives;

3rd, of all possible tri-derivatives only mesitylene and pseudocumene are present;

4th, all three xylenes occur in tar-oil.

(The last is made clear by the graphic reaction schemes given in the original.)

Allylene has not yet been observed among the products of destructive distillation; but Jacobsen ascribes this to its easier condensation, and to the difficulty of discovering small quantities of it mixed with acetylene.

Even on Jacobsen's theory the formation of the other hydrocarbons occurring in tar can only be explained by elimination of hydrogen, as shown by Anschütz:[1]

$$5C_2H_2 = C_{10}H_8 + 2H$$
$$C_{10}H_8 + 2C_2H_2 = C_{14}H_{10} + 2H.$$

Anthracene and phenanthrene might also be formed by a condensation of ditoluene:

$$2C_7H_8 = C_{14}H_{10} + 6H.$$

It is an argument in favour of Jacobsen's theory that coal-tar has certainly been found to contain only methylated benzene homologues, exactly those mentioned by him, but neither cumene (isopropylbenzene), propylbenzene, nor ethylmethylbenzene. It is true that older treatises enumerate cymene (methyl-isopropylbenzene) as a constituent of tar, but upon insufficient evidence; so that nowadays cymene is not considered to be present in tar. But since K. E. Schulze has discovered tetramethylbenzene in coal-tar, Jacobsen's theory can no longer be upheld without some modification. K. E. Schulze himself[2] has originated another theory as to the formation of the hydrocarbons found in coal-tar. He believes the phenols to be the primary products, and the hydrocarbons to be formed from them by the splitting-off of the elements of water. This theory has obtained some support from the investigations of Kraemer,[3] Köhler,[4] and Staveley.[5] Watson Smith,[6]

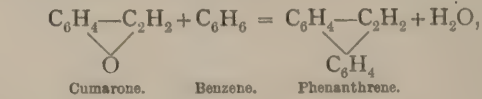
[1] *Ber.*, 1878, p. 1215.
[2] *Ann. Chem. Pharm.*, ccxxvii., p. 143.
[3] *Annalen*, clxxxix., p. 129.
[4] *Ber.*, 1885, p. 859.
[5] *Chem. Zeit.*, 1889, p. 1108.
[6] *J. Soc. Chem. Ind.*, 1883, p. 495.

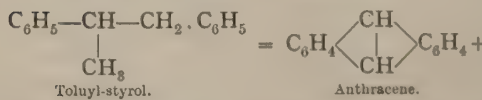
on the other hand, cites observations militating against at least its general application.

The hypothesis that acetylene is the principal factor in the formation of the coal-tar hydrocarbons does not harmonize very well with the researches of Vivian B. Lewes on the formation and behaviour of acetylene (1892), according to which acetylene is formed only at the highest temperature; while Bunte has proved (*J. Gasbeleucht.*, 1886, p. 595) that most of the tar is formed during the first hour of the distillation of coal—that is, at a comparatively low heat. According to Heintz (*ibid.*, 1886, p. 294) the temperature of the gas-retort during the first hour averages 420°, after 3 hours 960°, and after 5½ hours 1075° C.

Haber[1] believes that acetylene must play an important part in the formation of benzene. Heusler,[2] on the other hand, believes that benzene and its congeners are mostly primary products of the dry distillation of coal; he was led to this conclusion principally by his study of the behaviour of lignite and lignite-tar.

Kraemer and his co-operators[3] have adduced important objections against the theory that the *higher* aromatic hydrocarbons are formed from acetylene, and in support of the theory that they are formed from cumarone and styrol by condensing with the lower hydrocarbons, *e.g.*:

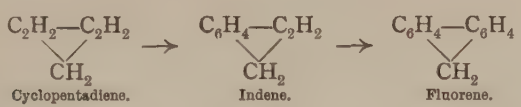


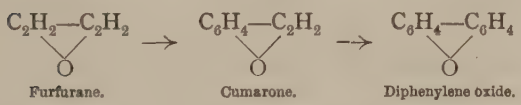


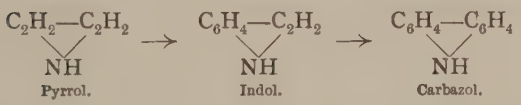
They believe[4] that the pyrogenetic products are principally formed from the original products of decomposition (methane, ethylene, acetylene, formaldehyde and ammonia), by polymerization and condensation with expulsion of hydrogen. As the process continues one or more acetylene groups are

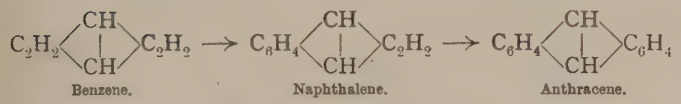
[1] *Berl. Ber.*, 1896, p. 2691.
[2] *Ibid.*, 1896, p. 2773.
[3] *Ibid.*, 1890, pp. 84, 3169, 3268, 3276.
[4] *Ibid.*, 1896, p. 552.

replaced by phenylene groups, and thus we obtain the following series:—









etc. etc. etc.

Probably none of the above-mentioned hypotheses can claim general application, and possibly all those reactions are concurrently at work in the formation of the exceedingly numerous constituents of coal-tar.

We will in conclusion quote the observation of K. E. Schulze,[1] that most of the tar substances belong to the *meta*-compounds, which are more stable than ortho- and para-compounds.

Russig (*Z. angew. Chem.*, 1899, pp. 948, 951) makes various objections to the theories of Berthelot, Jacobsen, and Kraemer, and develops a theory of his own, according to which the formation of coal-tar must be explained by the constitution of coal itself, and by the decomposition of the complicated cellulose molecules existing therein.

Vivian B. Lewes (*ibid.*, p. 826) points out that tarry matters are sometimes formed during the generation of acetylene from calcium carbide, and benzol can be proved in the scrubbing liquids, which facts point to the formation of aromatic hydrocarbons by polymerization of acetylene.

[1] *Ber.*, 1887, p. 409.

APPENDIX

Poisonous property of Coal-tar.

It is hardly necessary to say that coal-tar has strongly poisonous properties when it gets into the human body. But even its action on the skin is decidedly injurious, and leads to bad skin-diseases which are sometimes confused with the "acne," a sort of itch, occurring at electrolytic chlorine-works (where very much tar is used for protecting the apparatus). Russig, in *Chem. Ind.*, 1902, pp. 238, 432, has drawn attention to this. It is also treated by Ramboussek in a paper on injurious gases in industrial work (*Z. Gewerbehygiene*, Vienna, Vol. IX.). At paraffin works it is called "paraffin itch," and seems to be identical with the chimney-sweeps' cancer, several times mentioned in the English factory inspectors' reports. Especially in the manufacture of pure anthracene this troublesome disease has been frequently noticed, but by insisting on cleanliness on the part of the workmen it may be avoided altogether.

CHAPTER IV

THE APPLICATIONS OF COAL-TAR WITHOUT DISTILLATION

As we have seen on pp. 8 *et seq.*, considerable time elapsed after the successful introduction of gas-lighting before means could be devised for disposing of the tar obtained during the manufacture of the gas, or at least before it was regarded as a source of profit. Probably at that time the tar was burnt under the gas-retorts as much as possible, but this is not quite as easy as it might appear (see below), and only more recently the application of tar as fuel has been improved. Coal-tar was no doubt also employed from the first as a cheap paint for wood and metals, although it is but little adapted for that purpose in the raw state. But this would account for only a portion of the coal-tar obtained, and most of it remained a great nuisance to the gas-manufacturers, who had sometimes to pay considerable sums to get rid of it. This, no doubt, led to the first attempts at utilizing the tar by distillation, which we shall mention in Chapter V.

Before, however, gas-tar was distilled on a manufacturing scale in order to isolate the valuable substances contained in it, of course it had to be employed in other ways, either in the raw state or thickened by evaporation. Even later on the tar could not, and in some places up to this day cannot, be distilled to advantage, principally owing to the cost of carriage; and it was necessary to find other uses for it, in order to get rid of it.

Recently, as we have seen above (p. 155), the great fall in the prices of coal-tar products has led to such a depreciation of coal-tar itself that the question of disposing of it in other ways than by distillation has become much more urgent than before.

We shall in this chapter describe such applications of coal-tar as are made without submitting it to a proper distillation,

consequently either in the entirely raw state or merely deprived of water (and necessarily at the same time of its most volatile constituents) by preliminary heating.

Employment of Coal-tar for the manufacture of Gas.

This can be effected by passing the tar through red-hot tubes, or by heating it in a still and treating the vapours evolved in the manner just mentioned. This was the intention of the process of Koechlin, Duchatel, and Perpigna,[1] that of A. Bernard[2] (who ran the tar upon the coke remaining in the gas-retorts), that of Droinet[3] (who moulded the tar, mixed with ashes, coal-dust, sawdust, clay, etc., into compact lumps which were heated in ordinary gas-retorts), and that of Isoard[4] (whose tar-gas, prepared by superheated steam, contained, according to Monier's analysis, 17·8 per cent. ethylene and 71·9 per cent. "light hydrocarbon," *i.e.*, methane—which seems very doubtful). Similar processes are indicated in the B. Ps. of Hengst, Watson, Muschamp, and Wilson (1858), and that of MacCracken, Newton, Kirkland, and Husson. Still and Lane (B. P., 6th October 1871) mixed tar, together with some vegetable matters, with gas-coal. According to Bunte[5] all these endeavours led to nothing, as those substances which, by decomposing at a high temperature, furnish permanent gases are present in coal-tar in too small a quantity. Nevertheless fresh attempts will be made in this direction now that tar is of so little value. It is true that raw tar seems very badly adapted to gas-making, since the pitch, which forms the greater part of its bulk, is almost devoid of light-giving substances, and since, moreover, the pipes are very easily stopped up in the operation; but it is possible that tar deprived of its pitch, napthalene, and anthracene, as proposed by G. E. Davis, would be a suitable material for the above purpose. Even this is contested by L. Wright, as we shall see at the close of the next chapter.

Bäcker,[6] who had obtained a Ger. P., No. 43096, for a process of mixing tar with coke-dust and introducing this mixture in small portions into a red-hot gas-retort, claims to

[1] B. P. of 1854.
[2] *Dingl. polyt. J.*, cxlviii., p. 292.
[3] *Ibid.*, cxlviii., p. 295.
[4] *Ibid.*, clv., p. 462.
[5] *Schilling's Gasbeleucht.*, 3rd ed., p. 231.
[6] *J. Gasbeleucht.*, 1887, p. 908; *Z. angew. Chem.*, 1889, p. 16.

have obtained excellent results, but Bunte (*J. Gasbeleucht.*, 1887, p. 105) most distinctly contradicts this.

Ellery,[1] who worked in an inclined cast-iron retort, obtained from a ton of tar upwards of 15,000 cub. ft. of 15-candle gas apart from coke and ammonia.

Hempel[2] proposed working up gas-tar in a Lowe's or Granger's water-gas plant.

Burns[3] distils tar, while blowing in steam, to dryness; the gases are made to enter into a heated chamber, where they are well mixed and then pass through red-hot pipes filled with charcoal, where they are decomposed into illuminating-gas. According to the quantity of steam, the gas turns out either of greater illuminating-power or of greater heating-power. One gallon of tar and two gallons of water furnish 700 cub. ft. of 16-candle gas. When distilling coal at low temperatures and treating the tar as above, one ton of coal is stated to furnish 21,000 cub. ft. of gas (?).

Merkens[4] injects a spray of tar produced by a steam-injector into retorts half filled with coke. John Smith[5] describes another process for turning tar into gas.

Grebel[6] made experiments on the production of gas from tar mixed with coke or sawdust. One hundred kg. tar with 100 kg. sawdust and 20 kg. coke yielded 76 cbm. gas, 55 of which must be attributed to the sawdust. One hundred kg. tar and 250 kg. coke-dust yielded only 21 cbm. gas. In order to produce the illuminating-power of one candle, we require 42·9 litres of the first, and 31·4 litres of the second gas, as compared with 10·4 litres ordinary coal-gas. Those tar-gases therefore possess only 25 to 33 per cent. of the illuminating-power of coal-gas. Leybold's experiments on the same subject[7] were equally unfavourable.

Much stir was produced at one time by the Dinsmore process (B. P. No. 7714, 1887 (amended 24th May 1890); No. 15852, 1887; No. 4885, 1888; No. 2096, 1888; No. 16194, 1888), on which Carr[8] and Watson Smith[9] have made reports. Its principal feature is: passing the crude coal-gas, inclusive of tar

[1] *J. Gasbeleucht.*, 1895, p. 117.
[2] *Ibid.*, 1887, p. 521.
[3] B. P. No. 14958, 1886; *Iron*, 1887, p. 521.
[4] *J. Gasbeleucht.*, 1819, p. 188.
[5] B. P. No. 7605, 1893.
[6] *Dingl. polyt. J.*, cclxvii., p. 32.
[7] *Ibid.*, cclxvii., p. 32.
[8] *J. Soc. Chem. Ind.*, 1889, p. 960.
[9] *Ibid.*, 1890, p. 446.

and ammonia, from the gas-retorts into another retort heated by the same fire, and thus gasifying the tar by superheating. The volume of the gas is stated to be increased 10 per cent. and the illuminating-power to rise from 15 to 20 or 21 candles.

Kraemer's experiments[1] with the Dinsmore process led to a very unfavourable result. He found that the increase of volume of the gas is caused entirely by the decomposition of the methan and the olefines, the gas becoming much poorer in these and richer in naphthalene and phenanthrene. The decomposition of the benzenoid substances in the tar may be represented in the most favourable case as follows :—

$$4C_6H_6 + 2C_7H_8 + 2C_8H_{10} + 2C_9H_{12}$$
$$= 2(C_5H_5)_2 + 3C_{10}H_8 + C_{14}H_{10} + 2CH_4 + C_2H_2 + 9H_2$$

leaving the extensive separation of free carbon out of consideration. In 100 kg. of tar only 2·5 kg. benzenoid substances are contained, which, if decomposed as above, would account for an increase of 0·66 per cent. of the volume of the gas. The increase would rise to 1 per cent. if the phenols were decomposed in the some manner. Naphthalene is hardly changed; the heavy oils are also very persistent against heat, and at most split off a little hydrogen and methan. The pitch and soot contained in the tar have no action whatever. Hence the Dinsmore process effects nothing else than a hot distillation of the coal, viz., increased production of gas, diminished illuminating-power, obstructions by tar in the rising main and by naphthalene in the gas-pipes.

Exactly the same negative results have been obtained by the Deutsche Continental Gas-Gesellschaft[2] with the Dinsmore process.

Watson Smith (cited above) compared the composition of tar, obtained from the same coal by the Dinsmore process and by the ordinary process, with the following result :—

	Dinsmore Tar.	Ordinary Tar.	
Water . . .	1·1	7·1	per cent.
Light oil . . .	1·3	5·4	„
Creosote oil . .	16·5	17·8	„
Anthracene oil .	12·1	8·6	„
Pitch . . .	69·0	61·0	„
Sp. gr. of tar . .	1·157	1·150	„

[1] *J. Gasbeleucht.*, 1891, p. 225; *Fischer's Jahresber.*, 1891, p. 47.

[2] Priv. comm., by Dr Bueb, Dessau.

The creosote oil (containing about 50 per cent. naphthalene) showed :—

Sp. gr. . . .	1·030	1·025	
Crude carbolic acid	2·5	5·7	per cent.
Anthracene (pure) .	0·79	0·32	„

Hence there is no improvement in the quality of tar; any increase of the anthracene is more than made up by loss of benzol.

Rincker and Wolter (Fr. P. 391868, of 1908) introduce tar into a red-hot gas-producer. The gas formed here is partly carried away by its own pressure; the remaining tar vapour is forced by a current of air into a second producer and is there converted into a permanent gas. At the same time a blast of air brings up the first producer to a red heat, and the process is reversed by introducing tar into the second producer.

A plant for enriching water-gas by the products of the destructive distillation of coal-tar has been lately erected at Hythe, in the county of Kent (*J. Gasbeleucht.*, 1908, p. 110). The gas-producer contains a layer of coke, 4 ft. 8 in. deep, and is worked by draught, produced by a water-cooled steam-jet exhauster in the outlet chimney. The tar is introduced in the hottest part of the producer by two opposite tuyeres, placed underneath a small arch, so as to create a very hot free space. It is injected under a pressure of 0·4 atmosphere, by turns on opposite sides, 1·3 gall. of tar to 1000 cub. ft. of gas. The gas is enriched by benzols, injected from above by means of a pump, using 2½ lb. to each 1000 cub. ft. One man can serve two such producers.

Altogether the most competent judges agree in considering the manufacture of illuminating-gas from tar as a hopeless matter, which, however, will not prevent its being continually revived by new inventors.

Burning Tar as Fuel.

Where all other employments fail to procure a satisfactory outlet for the tar, it must be burned; and this is mostly done under the gas-retorts themselves. Its heating-value is, in this case, stated to be one and a half, or even twice that of coke;

but this is too much, as we shall see below. This employment of tar has always been the only practicable one where the distance of the gas-works from tar-distillers was too great and other uses of tar were too scanty; and during the last great fall of prices the burning of tar as fuel for the retorts has come to the fore again, even in some of the manufacturing centres, where such a process a few years ago would have been thought a ridiculous waste. In 1901, Russig (*Chem. Zeit.*, 1901, p. 90) stated the fact that at that time thousands of truckloads of tar were burnt, either in the raw state, or merely freed from water, ammonia, and the lightest oils by settling out or by a preliminary heating.

The simplest way of burning tar is by mixing some of it with coke. W. Bäcker (*J. Gasbeleucht.*, vol. xxix., p. 338) runs tar into the fireplace, about 16 in. below the surface of the coke, and finds that he can thus burn about 1 lb. of tar to 4 lb. of coke. This is also the plan most usually adopted at English gas-works; but it appears that much less tar is burned here in proportion to the coke. Mr Trewby states the quantity of tar used at the Beckton works = 5 gall. per ton of coke (*J. Soc. Chem. Ind.*, 1886, p. 563). Mr Wright (*ibid.*) also considers this to be the best way of burning the tar.

We shall describe some of the most suitable arrangements for burning tar, which equally apply to any liquid or easily liquefiable products of the distillation of tar for which no other outlet can be found (as is occasionally the case with some descriptions of "heavy" or "dead" oil), also to petroleum-residues and the like. We therefore take our descriptions partly from such places where as yet no tar, but petroleum-residues are burned, as they may be useful for tar as well.

That this subject has recently become of greater importance than previously is best shown by the large number of new patents taken out during the last few years; but we shall more particularly enter upon the description of apparatus seen working on the spot by competent observers.

So long ago as 1862,[1] patents were taken out in the United States by Bidley, by Shaw, and by Linton, for the use of liquid fuel; in 1864 an apparatus, by Richardson, was tried at Woolwich. Aydon and Shpakovsky, in 1865, devised arrange-

[1] Redwood, *J. Soc. Chem. Ind.*, 1885, p. 78.

ments for injecting the fuel as a spray, the former using steam, the latter a blast of air. Watson Smith used steam to inject creosote oil for boiler fires about 1867. In 1867, at the request of Napoleon III., H. St Claire Deville constructed an apparatus, which, however, proved a failure on being put to a practical test in Russia. Audouin, in 1869, invented a more suitable burner. Other more successful burners, which are now being used in Southern Russia, date from 1870 and later.

The simple plan of dropping tar into a hot fireplace is unsatisfactory; the combustion is very incomplete, and the consequence is that clouds of dense black smoke are sent forth (such as are seen hanging over the primitive Tatar distilleries at Baku), along with a very disagreeable smell of partially-burnt tar or petroleum. Hence special means must be employed to prevent these drawbacks. We shall enumerate, in the following, only the more important of the very many different descriptions of apparatus invented for this purpose.

An arrangement for burning tar, which answers its purpose fairly well, is shown in Fig. 28: *a* is an iron tank for tar (creosote oil, etc.), which runs in from a tap (*b*), best constructed as an automatically-acting ballcock, so that the level shall remain always the same, and the tar run off in a uniform stream through the pipe and out of the tap *c*, in an open jet (so that any choking-up can at once be observed), into the funnel *d*, and from this into a horizontal iron tube (*g*), which ends inside the fireplace. In the centre of the tar-pipe is a steam-pipe (*f*), which first passes as a worm (*e*) through the tar-tank *a*, and keeps it always warm. A cock (*f*) permits the regulation of the steam-jet, which, as it issues in the centre of the extremity of the tar-tube, converts the tar into a fine spray, and at the same time, acting as an injector, carries in through the open space *h*, which surmounts the pipe *g*, the air necessary for combustion. Thus the tar is brought into very intimate contact with air, and is almost instantaneously burned; a little of it falls down upon the plate *i*, where it burns into coke, which is removed from time to time through *k*.

Fig. 30 shows a contrivance for burning the tar without a steam-jet, by Liegel,[1] specially intended for heating gas-retorts by tar. The tar drops through an opening (*a*) $1\frac{1}{4}$ in. wide,

[1] From Schilling's *Gasbeleuchtung*, 3rd ed., p. 325.

upon a plate (*b*) 5 ft. 3 in. below, which reaches through the front wall and is shut off by the door *c*. The latter consists of a slide, moving air-tight on its bed by means of a screw. The air for combustion enters below the slide, and first meets a bed of red-hot tar-coke, collecting on *b*, which it burns into light-grey ashes. The tar is partly burned by the radiated heat

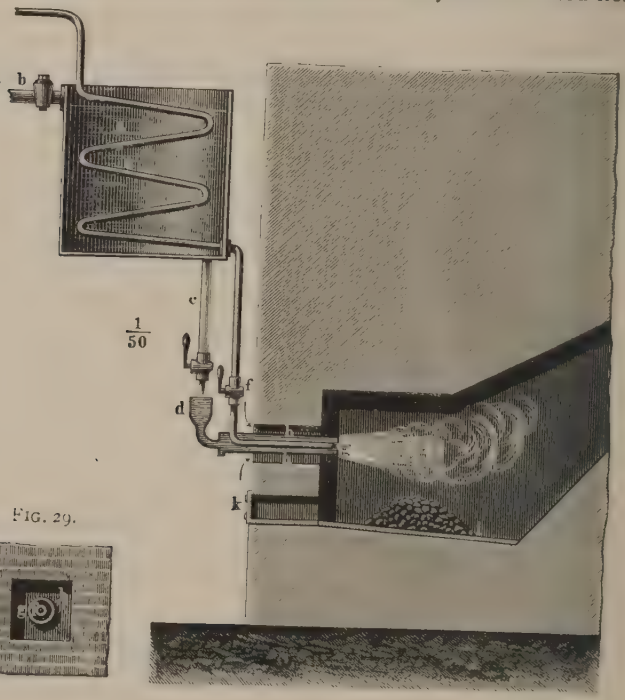


Fig. 28.

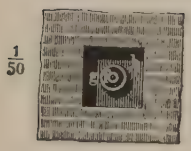


Fig. 29.

of the fireplace; but most of it falls on to the tar-coke burning below, is spread out, and meets the air coming in from the door-slide. The small door, *c*, is opened every half-hour for loosening the coke and getting out the ashes. Another door (*d*), with a peep-hole, is placed higher up, and is likewise to be closed air-tight.

Schilling (*ibid.*, p. 324) also figures a special "squirting-cock" for the tar, shown in Fig. 31. The vertical branch *a* is

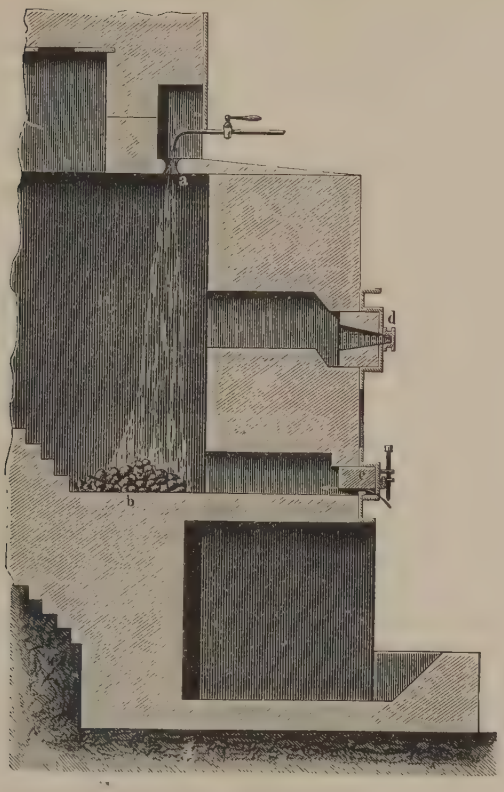


FIG. 30.

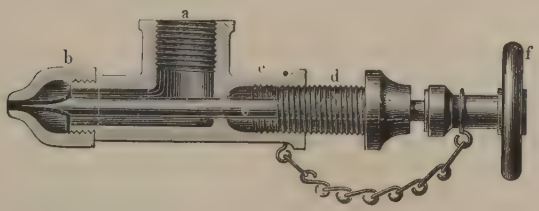


FIG. 31.

screwed upon the tar-supply pipe. The end turned towards the furnace is closed by a cap (*b*) with an opening about $\frac{1}{16}$ in. wide. The other horizontal end (*c*) is provided with a gland through which passes a long screw (*d*), which carries a horizontal needle (*e*). The outer end of *e* is provided with a small wheel (*f*), and is fixed by a small chain. The needle serves for partly or entirely closing, the opening (that is, for regulating the jet of tar), also for cleaning it out in case of need. The apparatus is fixed in the furnace-front, so that a slide can be put in front of it. In the case of gas-retorts there ought to be on the fireplace-bed a 4-in. layer of red-hot coke, which is broken up every half- or three-quarters of an hour. This bed ought always to be dry; otherwise too much tar has been run in, or too little air has been admitted. For the purpose of making a start, a small wood-fire is made on the hearth and the tar is run in at once.

H. T. Litchfield and D. Renshaw (Ger. P. 17659, of 1881) have constructed a special kind of nozzle for blowing in a mixture of the combustible liquid with air and steam, in such a way that a converging whirl is caused which intimately mixes the liquid with the air.

Another mixing-apparatus, evidently intended more for petroleum, has been patented by the Boston Petroleum Heating Company (Ger. P. 21648, of 1882).

O. D. Orvis[1] (Ger. P. 28017; in England patented as a communication to A. T. Boult, No. 5357, 1883) patents an apparatus, the essential novelty of which is a retort fixed to the inner end of the inlet pipe, in which any less volatile portion of the oil blown in may collect and may be vaporized by the fire; also a horizontal nozzle through which the mixed stream of steam, hydrocarbon, and air may issue in a sheet-like form.

R. B. Avery (B. P. 5795, of 1883) fits the oil-supply pipe with a series of perforated diaphragms of gradually decreasing mesh, in order to "atomize" the oil before it enters the steam-pipe.

J. H. Selwyn (B. P. 2160, 1884) burns liquid hydrocarbons in conjunction with water-gas or steam in presence of a

[1] This and a number of other apparatus are described and figured in *Dingl. polyt. J.*, vol. cclviii., p. 418, and in Wagner-Fischer's *Jahresbericht d. chem. Technologie* for 1885, pp. 1313-1318.

substance containing both carbon and iron, preferably employing plumbago, in a furnace specially described.

J. Leede and G. H. Ouray (B. P. 1864, 1884, a communication to W. P. Thompson) mix the liquid hydrocarbons with earthy matter, and describe special apparatus for feeding, igniting, and consuming that kind of artificial fuel.

J. D. Bodwell (B. P. 7615, 1885) employs a closed chamber fitted with shelves, sloping downward from the sides; the oil or tar falls from shelf to shelf, burning during its passage (*cf.* Nobel's shelf-burner, later on).

H. de Bray and C. D. Rosetti (B. P. 12990, 1885, a communication to J. Imray) fix to the crown of the fire-flue of an ordinary Cornish boiler a retort, into which oil or tar is admitted; a pipe leads the oil or gases to a receptacle on the fire-bars, to which a supply of air under pressure is also admitted.

A somewhat similar apparatus has been patented by P. Tarbutt (B. P. 5599, 1886).

J. Buffett (Ger. P. 30995, 1884) uses the steam first for heating up the oil, before it serves for converting it into a spray.

E. C. Burgess (Ger. P. 29614, 1884) avoids the use of a steam boiler by generating the steam, required for producing the spray, from liquid water, by means of a worm and retort fixed within the firebox.

J. B. Archer (B. P. 6347, 1886) patents an apparatus for firing steam-boilers by means of liquid hydrocarbons which are not "atomized," but are previously gasified.

William de St Martin (Ger. P. 36134) decomposes mineral oils along with steam in a red-hot retort, and mixes the resulting gases by means of an Archimedean screw previous to burning them.

W. Horn (Ger. P. 36403), in lieu of the fire-door, fixes a box provided with an inlet-spout for tar and a dish for spreading this out.

P. Mörth (Ger. P. 38166) sprays the tar by means of superheated steam.

Key (*Engineering*, 1886, p. 750) burns the tar after filtration without compressed air or steam.

Westphal's naphtha burner[1] is specially adapted to a

[1] *Dingl. polyt. J.*, cclxiii., p. 373.

blacksmith's forge-fire. The liquid fuel issues from a group of annular slits, and is sprayed by compressed air. The flame is directed upon the object to be heated by means of a beak-shaped jet. (This apparatus will probably do well for petroleum or creosote only, but would be stopped up too easily when burning raw tar.)

Rispler[1] puts the heating value of 100 coal-tar equal to 220 to 270 good nut-coal, and points out that the supply of air can be much more exactly regulated than with coal.

Descriptions of the burning of *petroleum-residues* at Baku (where they practically are the only accessible fuel) have been given by Boverton Redwood (*J. Soc. Chem. Ind.*, 1885, p. 78), and by C. Engler (*Dingler's polyt. J.*, cclx., p. 440, 1886).

According to Engler, these residues, called "massud" by the Tatar workmen and "astatki" by the Russians, form 55 or 60 per cent. of the crude petroleum. Some of it is used up for making lubricating-oils; but much more is burned, partly at the works, to supply the heat for distilling and for raising steam, partly as fuel for steamships and locomotive engines, even at a great distance, on the Caspian, the Black Sea, the Volga, on the Transcaucasian and Transcaspian railways, and so forth.

The heating-value is nearly twice that of coal; with burners of the best construction, one pound of massud will raise 12 pounds, or with care 14 or 15 pounds of steam. The distillation of 100 parts crude oil for kerosene consumes three or four parts of massud.

The burners for the residues, called "forsunka," have been principally introduced and improved by O. K. Lenz at Baku. They have very varying forms, but always work so that the oil is atomized by steam previously to burning. The atomizing by compressed air has not answered (*cf.* however, Nobel's shelf-burner as described below). Even with steam enough air enters to produce complete combustion, and a temperature beyond the fusing-point of wrought iron. Therefore the boiler-plates, heating-tubes, etc., must be protected against the direct action of the forsunka flame.

A very simple forsunka is shown in Figs. 32 to 35. The 1-inch iron steam-pipe D is flattened at its end to a slot of $\frac{1}{25}$ or $\frac{1}{50}$ inch width, through which the steam issues. The

[1] *Chem. Zeit.*, 1904, 957.

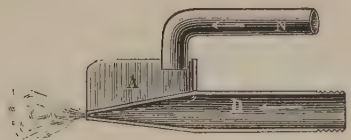


FIG. 32.

FIG. 33.

FIG. 34.

FIG. 35.

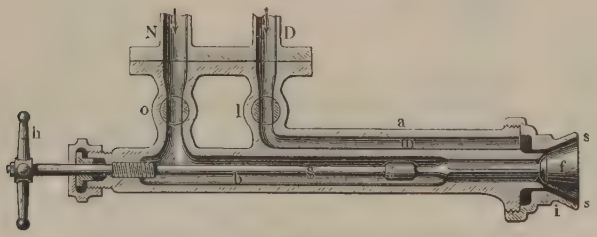


FIG. 36.

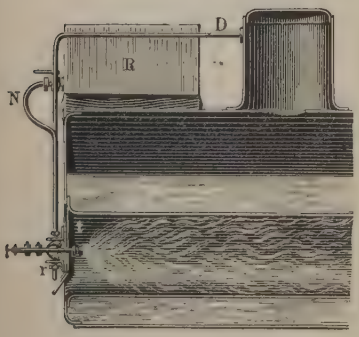


FIG. 37.

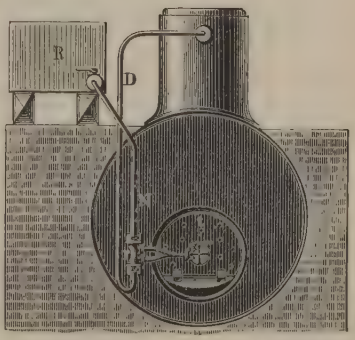


FIG. 38.

residues are conveyed by the pipe N; the thick oil spreads over the cup fixed over the steam-nozzle, runs down over the slit, and is converted by the steam into a fine spray. The different nozzles, shown in Figs. 32, 33, and 34, serve to produce a more pointed, or a broader, or a medium flame.

The Brandt forsunka (Fig. 36) somewhat resembles the spray-producer, or "squirting-cock" (Fig. 31, p. 255). The residues, arriving at N, and the steam from D, are separately carried forward in the tubes *b* and *m*, passing through the brass-casting *a*. The massud issues through an annular slit, regulated by the cone *f* by means of the handle *h* and spindle *g*; the steam issues by an outer annular slit, concentric with the former. Both are mixed between the cone and the nozzle *i*, and issue

FIG. 40.

FIG. 41.

FIG. 39.

at *s s* as a spray, which is lighted. The taps *o* and *l* are left open, the cone *f* serving to regulate the process.

Figures 37 and 38 show the application of such a burner to an ordinary Cornish boiler. The residue runs from the tank R through the pipe N into the burner; the steam comes from the dome D. At *r* the whole burner can be turned round in a horizontal plane, so that on turning it 90 degrees it is clear of the door *t*. In this position it is lighted, in order to prevent explosions, and is then turned back. The necessary air enters through the holes in the door *t*, and through a larger opening provided with a regulating valve.

The Lenz forsunka is shown in Figs. 39, 40, 41. The double brass-tube *a* a_1 (Fig. 39) ends in the cylindrical mixing-chamber *g*, closed at top and bottom by screw-lids *h h*; the movable rods *o o*, with the key-ends *p* and p_1, turn in bearings at *t* and *n*,

and end in eccentric pins (Fig. 40). The latter work in semi-cylindrical slides *e*, which are moved up or down by turning *p* or p_1, so that they more or less approach the midfeather *b*, and thus exactly regulate the supply of residues and of steam. The oil is converted into a spray, and issues as a sheet of flame through the horizontal slit *s*, which runs rather less than half-way

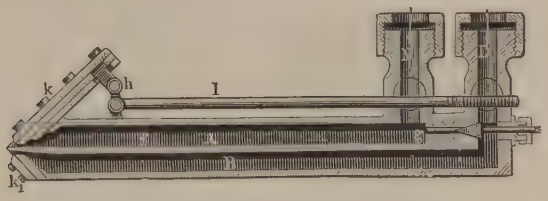


FIG. 42.

round the chamber *g*. D and N are taps for shutting off steam and oil. This kind of burner consumes about 3 to 3½ kg. residues, of specific gravity 0·910 and 140° inflaming-point, per horse-power and per hour.

Sandgreen's burner (also used by Nobel Brothers) is shown in Fig. 42. N and D carry oil and steam into the two halves of the chamber A B, separated by the partition *f*. The supply of

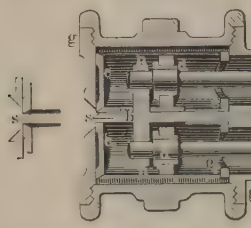


FIG. 43.

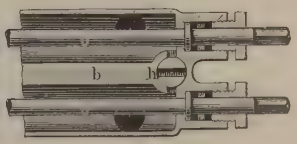


FIG. 44.

oil is regulated by adjusting the mouth-plate *k* by means of the lever *h l*, the supply of steam by the mouth-plate k_1 set once for all. The cone *m* permits occasionally cleaning out the compartment A by steam issuing through *g*.

A different description of burner must be used for locomotive and other tubular boilers, where the flame must be spread out. A Lenz burner for this purpose is shown in Figs. 43, 44, 45, 46. It is very similar to the other Lenz burner, Figs. 39-41,

but the slit *s* runs round the whole chamber *g*, except where it is joined to the burner, so that the spray issues in an annular form. Hence the slides *e* and e_1 must also be cylindrical, and must move up or down the chamber *g* like pistons. The

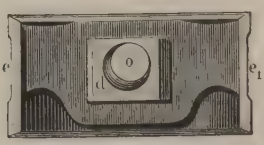


FIG. 45.

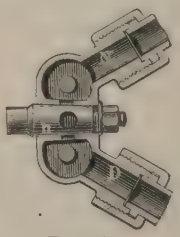


FIG. 46.

movement takes place by means of the rods *o*, running in bearings *n*, fixed to the partition *b*. When the eccentric rings *d*, attached to *o* (Fig. 45), are turned, the cylindrical slides *e* or e_1 are raised or lowered, and thus admit more or less steam or

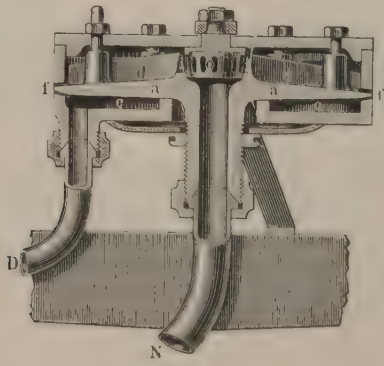


FIG. 47.

oil through the slit *s*. Fig. 46 is a vertical section through the supply-pipes, D for steam, and N for naphtha, etc. The tap *h* allows of sending steam into the oil-chamber for the purpose of cleaning it out. Fig. 44 shows a somewhat different shape of partition and burner mouthpiece.

Figs. 47 and 48 show a Brandt forsunka, as adapted to locomotive boilers. The mixing-chamber is divided into two

compartments by the horizontal disk *a*. Steam enters into the lower, smaller compartment through D; naphtha, etc., into the upper, larger compartment through N. By slightly turning the cap *o*, the slits *i i* are more or less opened, and the supply of

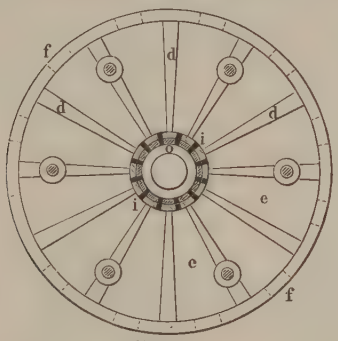


FIG. 48.

residues (naphtha, tar) can be thus exactly regulated. The latter issue radially between the ledges *d* through the sectors *e* and the slits *f*, and are atomized by the steam issuing below.

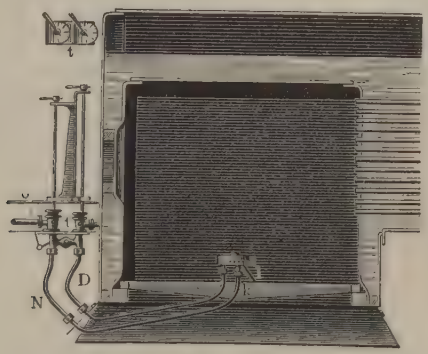


FIG. 49.

Fig. 49 shows the same burner (*l*), fixed in a locomotive fire-box in the centre of the grate (*k*). The consumption of naphtha for the transit of a train of twenty loaded trucks, according to Brandt, is about 10 kg. per km. (say 33 lb. per English mile).

Engler praises as advantages of forsunka-firing:—high

heating-power, small space for fuel, small volume of the burner, easy working, and, from his own observation, absolute freedom from black smoke in the case of factory chimneys. The locomotive fires are not quite exempt from smoke and smell, but more so than our own, worked with coal. Mr Redwood, in travelling on those lines, noticed no smoke, but occasionally a disagreeable smell of imperfectly burned petroleum.

The following astatki burners are mentioned in Redwood's description (*loc. cit.*). In Kaufman's burner (Fig. 50), which has

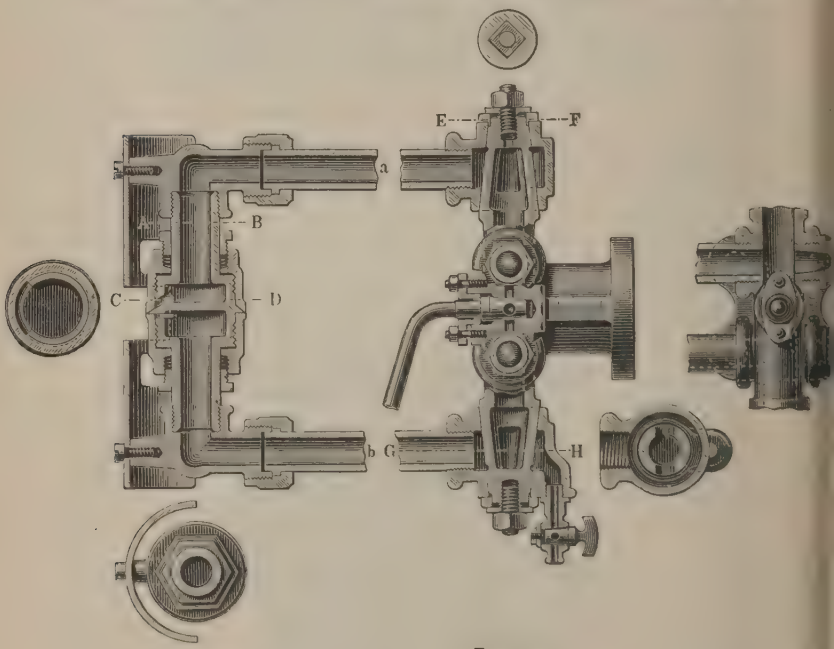


FIG. 50.

been adopted by the Russian Government for use in torpedo-boats, the oil enters at *a*, the steam at *b*; they meet at C D, where, by means of two screws, a fissure is opened through which they escape, a spray being produced. The intensely hot pointed flame makes it necessary to employ screens of fireclay in front of the boiler-plate. The roar of the blast is rather objectionable in this apparatus; but, nevertheless, more than a

hundred steamers on the Caspian and Volga are fitted with it. There are consequently no firemen or coal-trimmers, but a single attendant, whose duty it is to consult the pressure-gauge from time to time, and to regulate the supply of steam and astatki accordingly. In thus raising steam it is, of course, necessary for a start to take a supply of steam for the blast from a small auxiliary boiler, or to raise steam by an ordinary fire of wood or coal.

In consequence of the objections attaching to the steam-spraying method of burning astatki, Messrs Nobel have patented an apparatus free from them. This apparatus, as shown in Figs. 51, 52, and 53 (Fig. 51, a vertical section; Fig. 53, a sectional plan; and Fig. 52, a view of the boiler in front: more details of the plant are given by Redwood, *loc. cit.*), essentially consists of a series of troughs so arranged at the mouth of the furnace that the burning astatki flows by successive stages from the highest to the lowest. Air passes in between the troughs and through the four openings, *c*; the direction of the flame is given by the firebrick walls, *d d*. With this apparatus 14½ lb. of water can be vaporized by the combustion of 1 lb. of astatki, against only 12 lb. by the "spray" method.

Most remarkable results have been obtained with Nobel's trough-burner for metallurgical purposes. It reduces wrought iron to a state of fusion; and horseshoes, spanners, toothed wheels, and other articles of soft iron can be thus easily and cheaply produced by casting in moulds, without any heating of the air-supply. With this, no doubt, much higher temperatures might be reached; but the difficulty of finding materials sufficiently fireproof for the furnace stands in the way of making experiments in this direction. The freedom of this fuel from phosphorus and sulphur is a great advantage in metallurgical operations. The price of astatki in 1884 was 2s. 6d. per ton at Baku, or about 8s. per ton at Tsaritsin on the Volga; it is largely used in Moscow, and goes as far as Stockholm and Teheran.

So far as the use of this fuel for steamships is concerned, the economy of space for storage, and the saving of labour and time in placing it on board ship, must be taken into consideration. At the present price of coal-tar it would perhaps pay to use it for other purposes besides heating gas-retorts, in the

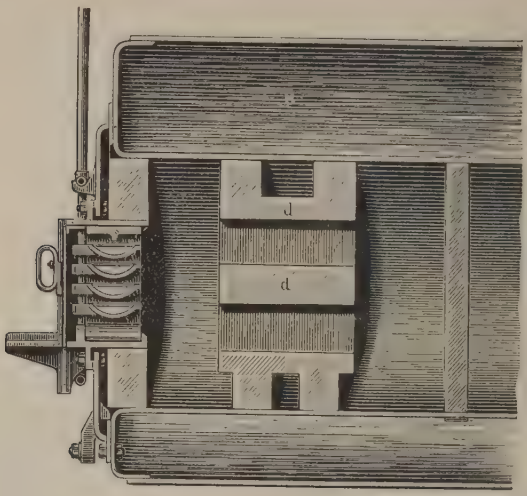


FIG. 51.

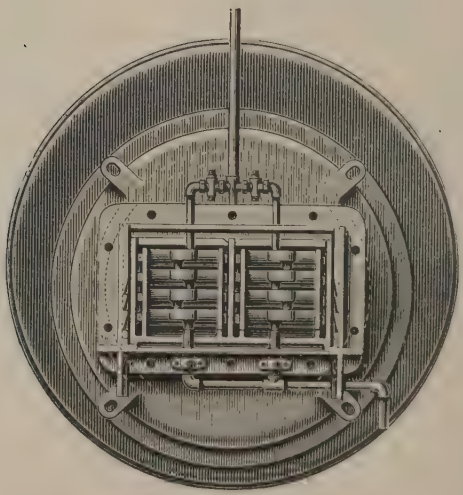


FIG. 52.

same way as astatki, wherever very great heat or economy of storage is of permanent importance.

Körting's steam-jet spray-producer (*Dingler's polyt. J.*, vol. cclx., p. 411) is much employed. This apparatus, shown in Fig. 54 (p. 268), is made entirely of iron, and therefore very substantial and very cheap (£3). It is claimed that the peculiar kind of steam-supply prevents any trace of tar from falling down. The supply of tar is regulated by a nozzle (A), more or less bored out; it is not easily stopped up, as a strainer (T) and sieve (S) retain the impurities. It is also readily accessible for

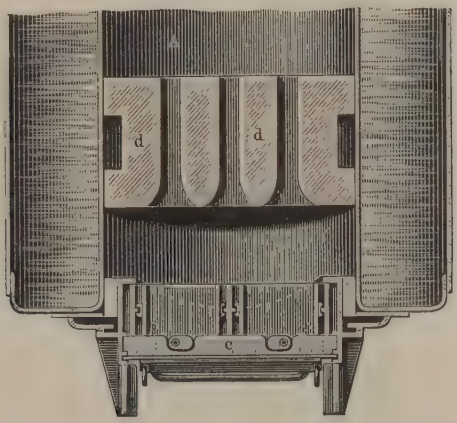


FIG. 53.

occasional cleaning by moving up the thimble H. The spray-producer itself can be cleaned any moment by means of the pin R, after removing the cover V. The steam-jet draws air through the box, L, with very great force; the slides, M, serve for regulating the air-supply. The steam enters through D, and the speed of combustion is regulated by means of the steam inlet-valve. The tar-cistern is placed on the top of the retort-furnace, so that the tar is always heated and thin.

W. Horn (Ger. P. 36403) patents a simple apparatus for burning tar, etc., which can be hung from the fire-door hinges, and is thus easily put in or taken out when a change from liquid to solid fuel is required.

Holden[1] has adapted the process of burning liquid fuel to oil-gas tar and successfully applied it to the steam-boilers and

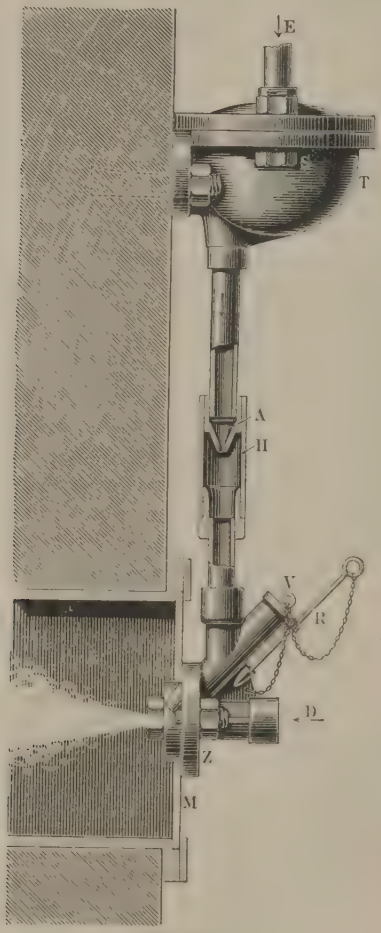


FIG. 54.

a number of locomotives on the North-Eastern Railway. He maintains on the grate a 3-inch layer of coal, over which the

[1] *Z. Verein. deutsch. Ingen.*, 1891, p. 496.

liquid fuel is sprayed by two steam-injectors (Fig. 55); a second annular steam-jet carries the air necessary for combustion into the firebox. If for some reason the employment of liquid fuel is to be discontinued, coal can be fired without any trouble. The only change to be made in a locomotive to adapt it for liquid fuel is to fit underneath the fire-door two pieces of 6-inch tubing, which pass through the water-space and the copper or iron back-wall of the firebox, and through which the fuel is blown in, as shown in Fig. 55. The steam is taken direct out of the boiler-dome, without overheating. Its supply to the tuyeres is regulated by a tap for both, that to the annular jets by special

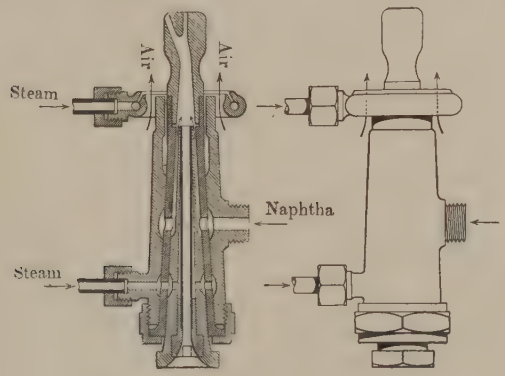


FIG. 55.

taps. A special steam-pipe (Fig. 55) admits of heating up the fuel in cold weather. All tar-pipes can be blown out by steam in case of obstructions. The greater part of the grate is covered with pieces of chalk or limestone, so as to admit but little air to the solid fuel from below. This system of heating requires only a slight draught, which has several advantages.

The Great Eastern locomotive shown in Fig. 56 (p. 270) possesses a tank holding a ton of tar, which suffices for a train of 15 carriages running 200 miles in suburban traffic. At the same time 25 cwt. of coal and ¾ cwt. of limestone are used, whilst with ordinary coal about 50 cwt. would be required. The saving in money is not considerable, but the advantages are that the combustion is smokeless, and the production of

steam can be at any time interrupted or started by means of shutting or opening the valves.

In 1902, Brückmann reports (*Z. Verein. deutsch. Ingen.*, 1902, p. 317) that the Great Eastern Railway of North America used Holden's plan in 88 locomotives, and consumed for this about

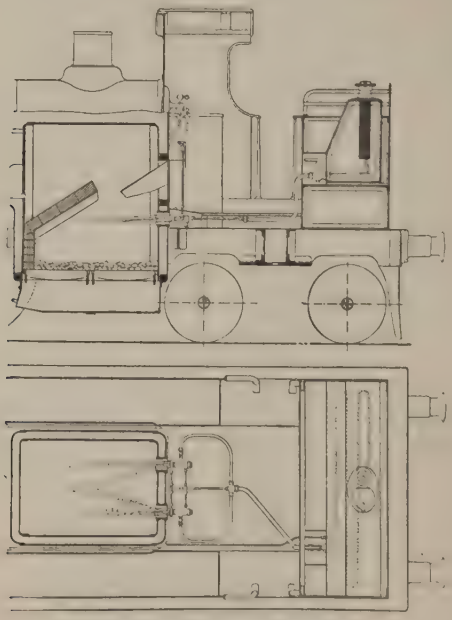


FIG. 56.

85,000 tons of tar—that is, about a quarter of the coal-tar then produced in the United States.

We quote also the processes of Busley (B. P. 5026, 1887), Mörth (Ger. P. 40142), Wrede (Ger. P. 56339), Heyden (*Chem. Trade J.*, 1887, p. 159).

In order to remedy the irregularity of flow produced by the impurities of raw tar, Livesey[1] inserts a number of pieces of $\frac{1}{8}$-inch brass tubing in the pipe between the tar-reservoir and the burner. This causes, by friction, a retardation and thereby a regulation of the flow.

[1] *J. Gas Lighting*, 1886, p. 159.

For a similar purpose J. Smith employs three lengths of tubing, 3 feet, 4½ feet, and 6 feet, coiled up into spirals, in order to provide for the changes in the fluidity of the tar and the temperature in the furnace; the level of the tar is to be kept 5 feet above the coils.

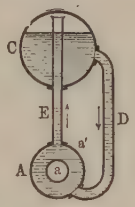


Fig. 57.

Seigle[1] objects to the employment of a single fireplace lined with firebricks. The flame produced by the liquid fuel is driven into water-jacketed tubes, acting like Bunsen burners, the combustion being commenced and finished in the interior, and colourless hot gases issuing from them, to be utilized elsewhere. As shown in Fig. 57, each tube (A) is formed of two concentric cylinders (*a a'*) with a common bottom. Above these is the steam-collector C, into which the feed-water is introduced by D to the lower part of A; tube E is the outlet for steam

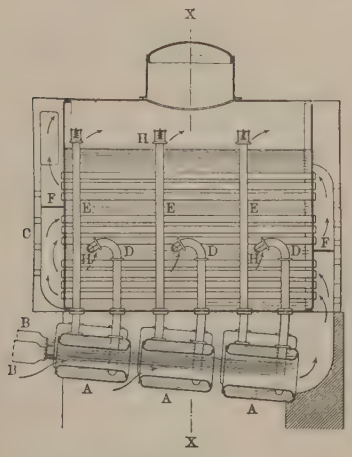


Fig. 58.

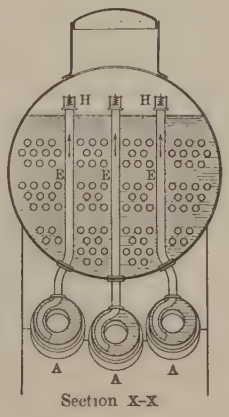


Fig. 59.

into the upper part of C. Figs. 58 and 59 show the application of this system to a ship's boilers. The apparatus consists of three rows of burners (A) connected with the main boiler by the feed-pipes D and the steam-pipes E. Opposite the first tube of each row there is a spray-producer (B), which drives a jet of

[1] *Zsch. f. Berg-, Hütten- und Masch.-Ind.*, 1895, p. 197.

lighted gas into three tubes (A), progressively enlarged so that the air for combustion is carried along through the annular free spaces between the tubes. The combustion must be regulated so that it is entirely or nearly complete when the gases issue at the end. They then rise upward and pass through the boiler-tubes, their course through the chambers C being shown by the partitions F. The last heat is applied to heating the feed-water,

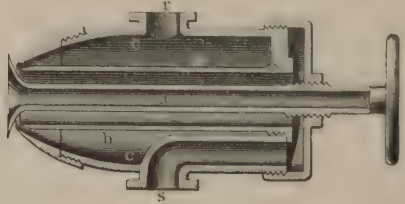


FIG. 60.

and the gases issue into the air without a chimney. The combustion of great volumes of gases and vapours in long and narrow tubes offers a good contact with cold surfaces.

Kämpf (Ger. P. 97505) avoids the necessity of using compressed air or steam by employing gases obtained in gasifying combustible substances and burning as well. The liquid fuel (Fig. 60) enters at *r* in a funnel-shaped orifice of the central

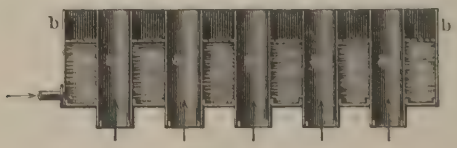


FIG. 61.

tube *a* of the set *a*, *b*, *c*, and is sprayed by the gaseous fuel entering at *s* and carried all round *a*.

Ferrari (Ger. P. 56240) avoids the use of spray-producers by a "box-grate" (Fig. 61), in which the grate is represented by channels, *a*, *a*. The fuel, contained below a perforated bottom (*b*) or supplied by perforated pipes, is drawn up to the surface of the burner by means of asbestos packing, acting like a wick.

The Relative Calorific Effects of Coal-tar (with and without Steam) and Coke, for Retort-firing.

At the meeting of the Gas Institute, London (*J. Gas Lighting*, 29th June 1886, pp. 1242-1244), a paper of peculiar interest at the present time was read on this subject by F. G. Dexter. To obtain the relative calorific values of tar and coke, Mr Dexter classified the constituents of tar according to their respective boiling-points under the different periods of distillation, and took the average formulæ of the hydrocarbons under these heads as representing the constitution of the oils obtained. The results appear in the subjoined table (p. 274).

Coke, when drawn from the retort and slaked, contains fully 25 per cent. of water, besides the ash and sulphur. Ignoring the impurities, and deducting 25 per cent. for water from the value of fired coke, $0{\cdot}75 \times 7000 = 5250$ units per pound of coke are obtained, or, in other words, a relative heating-value for coke and tar of 5 : 8.

By calculating the useful temperatures obtainable from both materials, Dexter arrives at a ratio between tar and coke = 2 : 1 ; but the elements of this calculation are not quite certain, and we would rather act upon the conclusion taken from practice that the above really represents the respective heating-values of tar and coke.

The practical heating-value of tar is due chiefly to its form and the ease with which it is manipulated. It can be introduced in a small constant quantity, and in a condition much more favourable for intimate mixture with the supply of air than is possible with coke, and consequently the excess of air supplied may be much less. The intermittent cooling produced by fresh charges of coke is also avoided, and thus a much higher heating effect is necessarily produced. The use of steam with tar should be avoided if possible, as it tends to reduce the temperature in the furnace.

This subject is further illustrated by a paper on "The Utilization of Residual Products in Gas-Works" (see *J. Gas Lighting*, 1886, p. 1247) by Mr J. T. Lewis. The author, in referring to the value of tar, shows that in 1883 the price varied from 1s. 8d. to 3s. 4d. per ton of coal carbonized, whereas at the present time tar is worth only 4d. to 7d. The following is the value of tar to tar-distillers, taking the prices of the different

Constituents.	Average Formula.	Weight per cent.	Boiling-point.	Proportionate Weight of Constituents.		Calorific Value.	
				Carbon.	Hydrogen.	Carbon Units.	Hydrogen Units.
First runnings	C_5H_{10}	3·0	up to 110°	0·025714	0·004286	200	148
Light oil	$C_{18}H_{14}$	7·0	110° to 210°	0·061091	0·008910	474	307
Middle oils	$C_{12}H_{20}$	27·0	210° to 240°	0·237073	0·032927	1842	1145
Heavy oils	$C_{14}H_{16}$	7·0	240° to 270° and upwards	0·063913	0·006087	497	210
Pitch (56 per cent.) composed of:—							
Oils	$C_{16}H_{10}$	17·5	360° and upwards	0·166336	0·008663	1292	298
Carbon	C	27·5	...	0·275000	...	2137	...
Gases and water . . .	...	11·0	...	...	...	...	...
				0·829127	0·060873	6442	2108
			Total . .	0·89		8550	

products at the current market-value. The various items are derived from two sources, one distiller carrying his process further than the other.

Products from one Still of 8 tons of Tar.

Naphtha, 60 gallons, at 9d. per gallon					£2	5 0
Light oil, 60 „ at 3d. „					0	15 0
Creosote, 500 „ at ¾d. „					1	11 3
Crude anthracene, 1 cwt.					1	11 8
Pitch, 5 tons, at 15s. per ton					3	15 0
Wages on the above			£2	0 0		
Coal			0	6 0		
					2	6 0
Wear and tear, rent, etc., not known						...
					£7	11 11

Giving about 19s. as the value of 1 ton.

Products from 1 ton of Tar.

Benzene (50/90)	5 gallons, at 1s. 5d. per gallon			£0	7 1
Naphtha	2 „ at 9d. „			0	1 6
Carbolic acid	5 „ at 1s. 8d. „			0	8 4
Creosote oil	50 „ at ¾d. „			0	3 1½
Crude anthracene, 30 lb., at 35 per cent.				0	8 0
Naphthalene	2 cwt., at 3s.			0	6 0
Pitch	11 cwt., at 9d.			0	8 3
Sulphuric acid, caustic soda, slack, and labour for working				0	10 6
Wear and tear, rent, etc., not known					...
				£1	11 9½

It is thus seen that tar is not at the present time very valuable to tar-distillers. In cases where the annual quantity of coal carbonized is below 30,000 tons, the distillation is said to be unremunerative. In considering the utilization of tar for fuel, the author gives the following particulars, illustrating the varying values of coke and tar in different localities:—

(1) Cost of coke for one furnace, per 12 hours		£0	7 4
Cost of coke and tar for ditto		0	5 2
	Saving	£0	2 2

Thus showing a saving of 4s. 4d. for each furnace per 24 hours.

(2) Coke saved in 24 hours, 1 ton		£0	16 8
Tar used, 90 gallons, at 1½d. per gallon		0	3 9

Thus showing a saving of 12s. 11d. per 24 hours. Value of tar as fuel up to 2d. per gallon.

(3) Coke saved, 13 cwt. at 4d., in 24 hours . .	£0	4	4
Tar used, 68 gallons, at 10s. per ton . . .	0	3	5

Thus showing a saving of 11d. for each furnace per 24 hours. Tar value, 12s. 9d. per ton.

When coke is selling at 5s. per ton, and tar at 7s., the one can be sold as profitably as the other; but in the majority of cases it will pay better to sell coke than tar.

Much less favourable as regards the value of tar are the statements of L. T. Wright (*J. Soc. Chem. Ind.*, 1886, p. 561), according to whom the proportion of steam raised in a Galloway boiler by coke (from Silkstone coal) and by coal-tar was only as 1 : 1·13; in firing the gas-retorts the proportion was 1 : 1·17 when atomizing the tar by steam, or 1 : 1·24 by gravitation feeding.

Wright subsequently[1] reports on comparative trials made for raising steam with coals, coke, tar, or creosote oil, continued for a period of forty-six days, with the following results:—

Class of fuel.	Number of days' trial.	Pounds of water evap. from 12° C. at 40 lbs. steam-pressure.	Pounds of water from 100° C. at atmos. pressure.
Notting Top Hard Cannel .	11	7·46	8·78
Silkstone Gas Coal . . .	7	8·42	10·01
Coke from Top Hard Cannel .	6	8·34	9·91
Silkstone Gas Coke . .	6	9·49	11·15
Tar steam injected . . .	7	10·70	12·91
Creosote steam injected . .	9	11·24	13·35

Later on he abandoned the injection by steam in favour of a simple apparatus, consisting of three fireclay slabs, placed in a slanting position in front of an ordinary coke-grate, with channels in between, through which the tar enters, together with air. The fixed carbon of the tar is burned farther on upon the grate. The draught need only be 2 mm. vacuum against 6 mm. for coke. If black smoke is avoided the smoke-gases contain on an average 12·9 per cent. CO_2.

Körting[2] also shows that it is even possible to replace two

[1] *J. Soc. Chem. Ind.*, 1887, p. 36. [2] *J. Gasbeleucht.*, 1886, p. 543.

parts of coke by one of tar as fuel. With a good (Muntz) gas-producer 100 kg. of Saar coal is distilled by means of 9·6 kg. coke, or 100 kg. of Westphalian coal by 12 kg. coke. These 9·6 or 12 kg., according to the caloric power of the substances in question, ought to be replaced by 8 or 10 kg. of tar, but Körting was never able to attain this. The principal difficulties are:—that the supply of air cannot be kept near the theoretical without danger of black smoke, and that previously-heated air cannot be employed, because this involves keeping the fire-door shut and prevents observing and regulating the flame. He considers the best plan that of spraying the tar by means of a Körting's injector.

Körting states that in 1886 forty-four German gas-works, producing nearly half of the coal-tar obtained in Germany, were burning tar, and were thus consuming 11,434 tons of tar, equal to 12 per cent. of the total German production. He states that nearly all English gas-works were burning tar equal to 20 per cent. of their total production; but this is contradicted by other authorities, quoting the tar burned only = 1 to 5 per cent. of the total (*e.g.*, Davis in *Chem. Trade J.*, 1887, p. 103).

Kraemer also considers that much more tar is burned in Germany than in England, and that the fuel value of 1·2 against 1 for coal is about right. He proposes burning only the tar from the hydraulic main and from the later stages of gas-making, and keeping the better quality for distillation.

James Hargreaves proposed burning coal-tar as a source of motive power in a specially constructed hot-air engine. According to the *Chem. Trade J.* of 11th June 1887, an engine with a working barrel of 25 ins. diameter and 18 ins. stroke gave 29·7 indicated h.p. with a consumption of 2 gall. of tar, that is an efficiency of 0·174, equal to the best gas- or steam-engines. Since then very little has been heard of this engine, but if it were successful the problem of disposing of the superfluous tar would be definitely solved.

Coal-tar is also used in conjunction with coke-oven gas, for *heating coke-ovens*. According to *Eng. and Min. J.*, 1904, p. 708, this has the special advantage that the heating-gases contain less sulphur. This latter circumstance is also of importance when using such a mixed gaseous fuel in Siemens-Martin steel-furnaces.[1]

[1] *Eng. and Min. J.*, 1904, p. 708.

Employment of Tar for preserving Timber, Stone, Iron, etc.

Coal-tar has always been extensively employed for the *preservation of building-materials* of all kinds. Stones as well as iron and wood can be preserved much longer, and protected against atmospheric influences, by a coating of coal-tar.

For *stones*, *brickwork*, *etc.*, especially when exposed to the action of acid vapours, Kuhlmann[1] strongly recommends painting with coal-tar. Long before that, however, it was usual in chemical works to boil the stones intended for erecting acid-tanks, hydrochloric-acid condensers, chlorine-stills, etc., in gas-tar somewhat boiled down, also to paint the brickwork of the furnaces and any wood or iron work exposed to acid vapours with coal-tar, nay even to soak the roofing-tiles in the same; and this is done up to this day. It has been noticed at the works that coal-tar not merely renders those objects less liable to be acted upon by damp, acids, etc., but makes the stones much harder and able to resist mechanical wear and tear. Hence the stones intended to be used for acid-cisterns and the like must be completely dressed by a stone-mason before they are put in the tar-pan, as they will not take the chisel after boiling. Fireclay pipes, which in the crude state are not even water-tight and are extremely fragile, after boiling in tar become acid-proof, hard, and very little sensitive to changes of temperature. But there is no reason why the employment of coal-tar in this direction should be confined to chemical works. It has been observed that brick-paving lasts very much longer if the bricks have been first soaked in hot tar. This is also the case with roofing-tiles, and is as good as, though very much cheaper than, glazing them, to make them stand the weather.

On my own recommendation, a large brick-works has extensively employed hot coal-tar for preparing black roofing-tiles, with complete success. But it must be noticed that a mere dipping in ordinary coal-tar is not sufficient to produce a permanent coating of adequate strength. The tar should be heated to at least 100° C., and the bricks or tiles, etc., should be left in it for some time, till, on breaking a sample, it is found to have rather deeply penetrated into the substance of the brick. The tiles are then left to dry for some time, isolated from one another on convenient frames.

[1] *Comptes rend.*, lvi., pp. 1006, 1146.

For all these purposes the tar should be deprived of water and of its most volatile oils by evaporation or (far more rationally) by heating in a still; and much the best is the varnish or "refined tar" made from pitch and tar-oil (comp. Chapter VI.).

Tar is also employed for *painting metals*. When laid on hot, as frequently practised by blacksmiths, it produces a shining and lasting black coat. Also cast-iron gas-pipes are mostly protected against rusting by a coat of tar laid on hot. That this is regularly practised in chemical works has already been stated. In such cases it does not matter if the coat is rather rough and thick. Should, however, a thin, equal, shining, and lasting coat be required, in the place of raw tar one of the varnishes made from pitch and tar-oils, which are described in Chapter VI., must be employed.

Before painting with tar, iron materials should, if possible, be heated, or else tar entirely freed from ammoniacal liquor must be employed, as the latter induces corrosion of the iron.

The Union of German Iron-founders prescribes that the iron pipes should be carefully cleaned, heated evenly to 150° C., and painted inside and outside with the tar-varnish, which must be heated up at least to 100° C. The coat of paint should be firmly adhering and tough.

When properly made, the protection of iron by purified tar (or, preferably, the tar-varnish described in Chapter VI.) is much better than by the ordinary red-lead and linseed-oil paint, which is not merely gradually destroyed in damp soil, etc., but according to Toch (*J. Soc. Chem. Ind.*, 1905, 527), gradually becomes pervious to water.

E. Fischer, in *J. Gasbeleucht.*, 1908, p. 1152, gives special rules for proceeding in tarring cast-iron pipes.

For *preserving wood*, coal-tar was recommended as early as 1799, by Le Bon; but for this purpose it is inferior to wood-tar, which even now is exclusively employed in shipbuilding. Wood-tar penetrates much more deeply into the pores of wood, covers it with a coherent coat, and the preservative action of its phenols is assisted by its paraffin. The drawbacks of coal-tar are its free carbon and its naphthalene. The former prevents the tar from entering the very finest pores; the latter, volatilizing even at ordinary temperatures, leaves gaps in the coat.

Some go so far as to say that coal-tar produces interior rotting of the wood; but this has not been positively proved, and the manifold employment of coal-tar in chemical works has never led to such a result. At all events the tar-varnishes are preferable to crude coal-tar for wood-painting also. *Tar-vapours* are said to act even better than tar in preserving the wood; this has been patented by Robbins in the United States and by Paradis in Austria;[1] the success of this process, however, is more than doubtful, as we shall see when treating of creosote oil. It is unnecessary to say that coal-tar is in any case very inferior to the "creosote oils" employed in the proper way for "pickling" timber, as will be described in Chapter VIII.

Rives[2] proposes as a substitute for wood-tar a mixture of coal-tar, rosin, and lime. A mixture called *sulphur-tar* or *benz-asphalt*, prepared by boiling two parts of sulphur with three parts of coal-tar, has been strongly recommended as protecting wood, iron, and stone against decay and rust. A similar mixture is the *wood-cement*, employed as a roof-covering (Chapter VI.). A mixture of coal-tar with its own weight of hydraulic lime, Portland cement, etc., is said to liquefy at 70°, and to yield on cooling a soft, pliable varnish, resisting acids and specially adapted for wood under water, water-pipes, and roofing-tiles (Dreyssig, Ger. P. 10685). Wildhagen (Ger. P. of 1885) recommends a mixture of wood-pulp, coal-tar, glue and water, employed in the cold state.

Employment of Coal-tar for the Manufacture of Roofing-felt.

Roofing-felt seems to have been introduced during the 18th century in Sweden by Faxa, and in 1791 in the Tyrol by Kag. Faxa simply covered the roof with millboard and then painted this with wood-tar. Kag prepared the millboard beforehand by impregnating with oil-varnish and dusting it over.

Soon a cheaper material was found in coal-tar, one of the first employments of which was for this particular purpose. In Germany it was first introduced in the beginning of the 19th century by Gilly, but without lasting success until about 1840, when several factories were established at Neustadt-Eberswalde and Leipzig, which were soon followed by others,

[1] *Wagner's Jahresb.*, 1871, p. 848. [2] *Dingl. polyt. J.*, clvii., p. 317.

so that the manufacture of roofing-felt in Germany, and later on in America, became a very important branch of industry, consuming large quantities of coal-tar and considerably influencing its price.

A historical survey of the employment of coal-tar for roofing-felt and for roof paints, which are frequently sold by fancy names,[1] is given in the *Asphalt- und Teer-Industrie Zeitung*, 1904, pp. 415 and 431. The consumption of coal-tar for this purpose is very considerable indeed on the Continent and in America.

Special investigations (*ibid.*, 1903, p. 67) have shown that the tar employed in this way is very gradually changed by evaporation, but not at all by oxidation.

The preparation of roofing-felt from single sheets of mill-board was soon replaced by that of rolls of great lengths, dispensing with all transverse joints on the roof, and producing a roofing-material of great durability and extraordinary cheapness.

The material for this manufacture is formed by rolls of mill-board made of pure wool fibre, about three feet wide. The tar must be pure coal-tar, freed from water. This was formerly effected by heating it in open pans, but is nowadays always done by distilling it in close stills up to the point where no more water comes over, with condensation of the benzol distilling at the same time. This "distilled tar" can be immediately employed for the manufacture of roofing-felt, and is greatly to be preferred to "prepared tar," that is, pitch dissolved in creosote oil. Roofing-felt prepared with the former dries much more quickly than that made with "prepared tar." But the latter is better than the former for painting the roofs when laid, simply because it contains fewer volatile constituents and keeps the roofs more elastic. Lignite-tar, oil-gas tar, or beech-wood tar can be used only when mixed with coal-tar or pitch.

The following is a description of a complete modern plant for the manufacture of roofing-felt, as built by Wilhelm Lückau, Hamburg. As seen from Figs. 62 and 63, a tar-still is fixed at

[1] Of such fancy names we will mention: lindol; firmatin; stegiol; sonnenkönig; solitect; excelsior protection; tectorial; hephæstos; furolin; lava saphire; eternol.

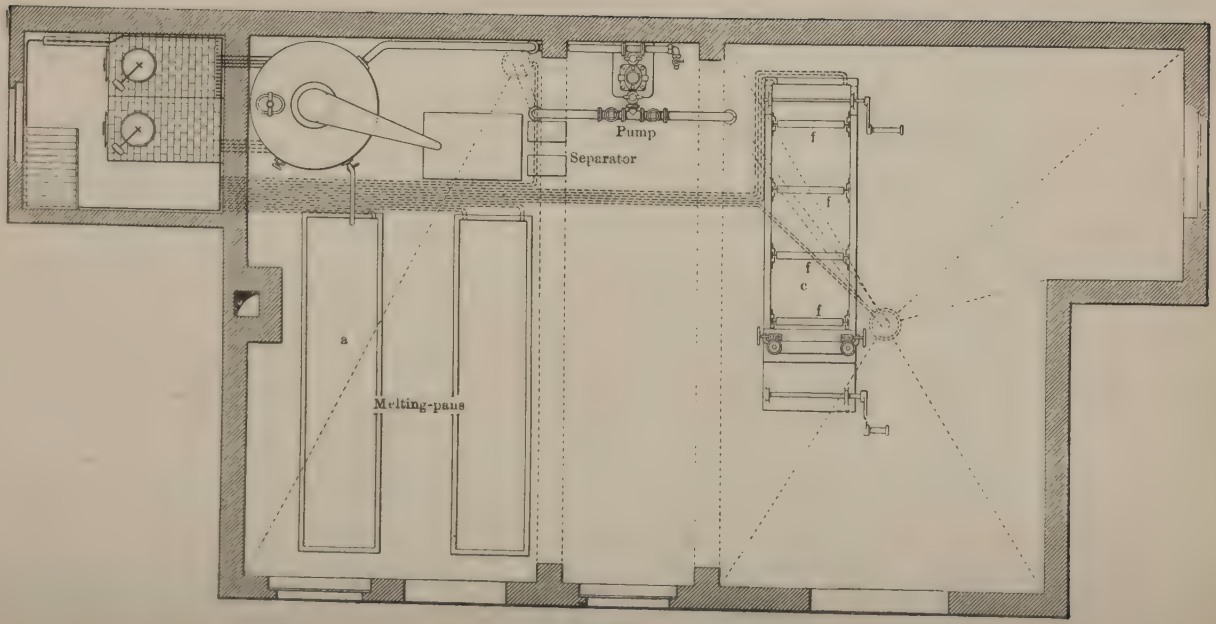


FIG. 62

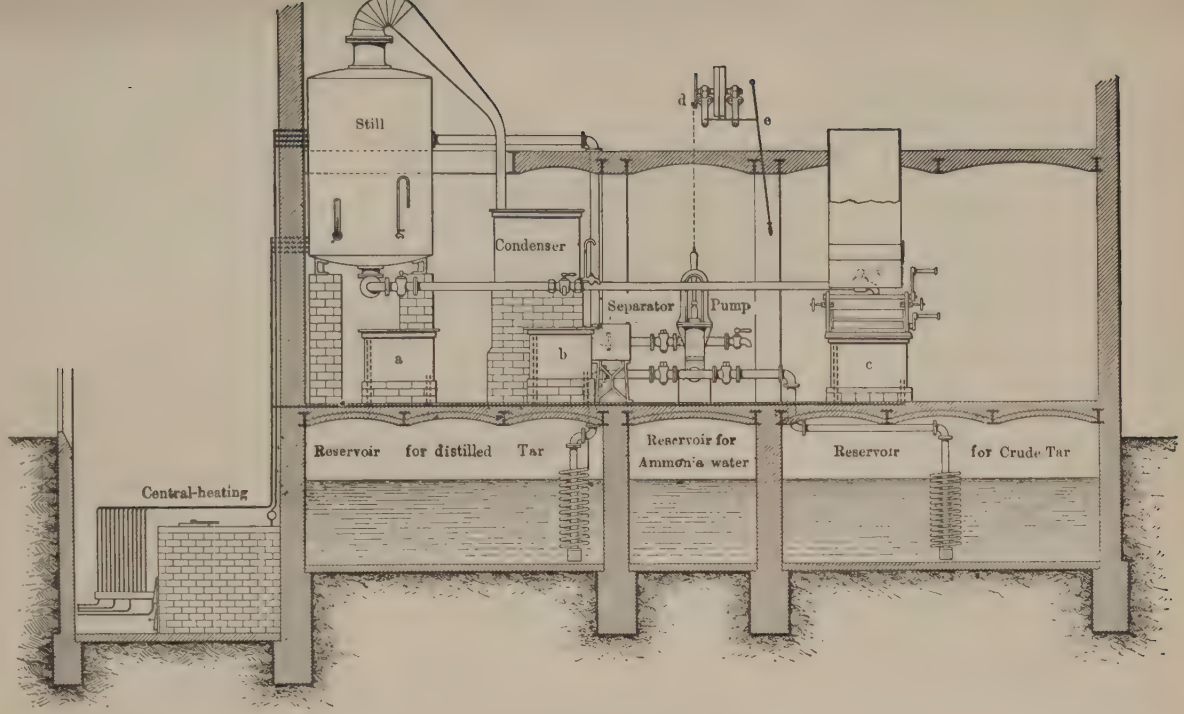

Still
Condenser
Separator
Pump
a
b
c
d
e
Reservoir for distilled Tar
Reservoir for Ammonia water
Reservoir for Crude Tar
Central-heating

FIG. 63.

such a height that the dehydrated tar can be run into the pans *a*, *b*, *c*, or a subterranean reservoir. The still, as well as all other apparatus, is heated by steam. The still is charged from the reservoir by means of a ram-pump, with gearing *d* and *e*, which also serves for another reservoir, containing distilled tar. A tank between these two receives the ammoniacal liquor distilling over. The benzol coming over at the same time runs straight into wrought-iron store-tanks. In order to guard against severe cold, the aspirating-pipes of the pumps are surrounded with heating-coils.

Pans *a* and *b* serve for preparing the cement required in

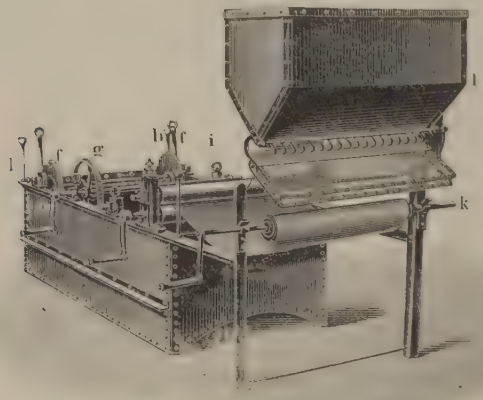


Fig. 64.

covering a roof with felt, also for wood-cement, etc.; the manufacture of the roofing-felt itself takes place in pan *c*. This is a wrought-iron box, 4 ft. wide, 13 ft. long, and 3 ft. 2 ins. deep, with a number of removable winding-drums or reels (*f*) for the raw felt. These drums are fitted on one side with a cog-wheel, in which another cog-wheel with hand-crank (*g*, Fig. 64) can be made to gear. Thus one reel after another is charged with felt. The pan is filled with tar to such a height that the felt is at least covered. The temperature of the tar should not be less than 95° or 100° C., because otherwise the felt absorbs too little and the surface becomes greasy.

From the drums the felt passes through squeezing-rollers (*i*),

which can be adjusted by a screw for greater or less distance (Figs. 64, 65). These rollers are made of iron, covered with felt, and are turned by hand. They serve both for taking the roofing-

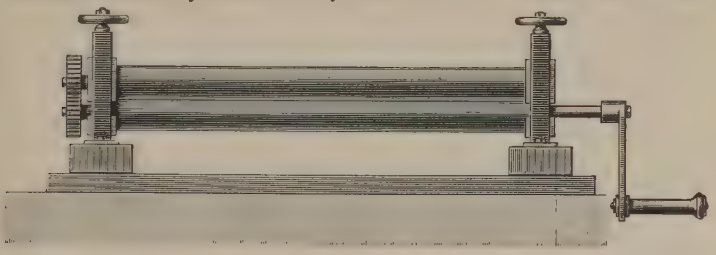


Fig. 65.

felt out of the pan and for removing the superfluous tar. Another wooden roller (*k*) with hand-crank serves for winding up the impregnated felt, after it has been dusted with sand. This roller consists of two portions, fitted together with a

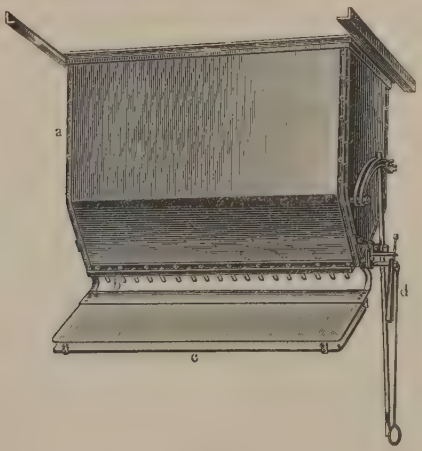


Fig. 66.

slanting joint, so that the felt can be freed by simply pulling asunder the two halves.

The dusting with sand is effected by the apparatus (Fig. 66), consisting of a sand-box (*a*), a spreader (*b*), and sieve (*c*). By *d* the supply of sand can be regulated at will or stopped.

All this machinery is worked by hand. Many attempts have been made to do it mechanically, but without success, as the loosened felt is not sufficiently resistant and the least irregularity causes it to tear, which is easily avoided by a careful man working by hand.

The raw felt is supplied in various strengths from 600 to 2000 superficial feet per cwt. The sand must be sharp—that is, of fine grain and entirely free from clay. It is first dried in the air or by artificial heat, and separated into various sizes by means of a cylinder-sieve. Where good sand is not obtainable, sifted coke-breeze, slag, etc., can be used. In some cases even sawdust is employed. Sometimes felt sanded on one side only or not at all must be made, in which case the squeezing-rollers are placed together as tightly as possible.

A detailed description of the manufacture of asphalt-pipes and roofing-felt, which does not essentially differ from the above, is given by Petersen-Kinberg in a booklet with the lengthy title: *Wie eine moderne Teerdestillation und Dachpappenfabrik eingerichtet sein soll*, Wien und Leipzig, 1904, pp. 164 *et seq.*

Roofing-felt is employed principally for roofs, either by itself or as a basis for slates or tiles; also for covering wooden partitions and for pipes exposed to the open air. It is frequently used for insulating brickwork against the humidity of the soil. This "insulating felt" is made from the strongest raw felt; the impregnating mass is made very thick. The squeezing-rollers are placed far apart, and the "sanding" is done with gravel the size of peas. This kind of insulation is preferable to the former method of pouring on a layer of asphalt, for when the brickwork settles down the asphalt splits and admits the moisture from below, whilst the felt adjusts itself to the changed conditions.

Recently attempts have been made to put the tar at once into the heating-engine where the felt is made, but nothing is known as to the result.

We quote a number of German patents referring to the manufacture of roofing-felt, or to varnishes for impregnating or covering it:—

Otto, No. 3141; Siebel, No. 43349; Jacobius & Sons, No. 54224; Kanert, No. 91809; Andernach, No. 92309; Wangenheim, No. 78047; Roedelius, No. 64680; Gentzen, No. 70852;

Richard, No. 73122; Joecks, No. 96094; Hatschek, No. 101453; Hoepfner, No. 103899; Dörr, No. 137507; Mathies, No. 163002; Nebeling (appl. B41262); Heilpern & Haas, No. 160660.

British patent: Walbinger, No. 11593, 1902.

Sommer has filed a patent application for the following apparatus (Fig. 67), for separating the water from tar without danger of fire. The tar is boiled in pan *o* till free from water, then by overheating *o* it is driven over into pan *o'*, so that the lighter portions collect in *o'* and the heavier ones (pitch) remain in *o*, from which they are run from time to time. In order to

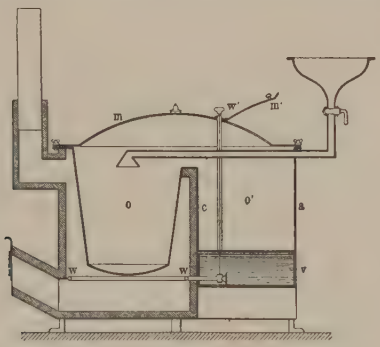


FIG. 67.

drive the tar from *o* to *o'* without danger of fire, *o* is surrounded by a double wall (*c*), which prevents any overheating on the outside of the pan. Underneath *a* is an annular spray-pipe (*w*, *w*), fed from the tank *v* and instantly started by means of *w'* from without.

Sometimes roofs made of tar-felt are subsequently painted with ordinary oil-paint. That is a mistake, unless the felt has been previously covered with an insulating layer of quickly drying varnish or of blood and slaked lime, which must be allowed to harden before the oil-paint is laid on.

Coal-tar as a Cementing Substance.

Raw tar is much less used for this purpose than pitch and other articles manufactured from it. It appears, however, in that function in a good many patents.

Formerly raw tar was frequently used for forming blocks from small coal, called *patent fuel* (*briquettes*). It has now been generally replaced for this purpose by pitch, which is much better suited for it, and of which we shall speak in Chapter VI. A new German patent (No. 170979) in this line has been granted to Shedlock. Possibly that is the process mentioned in *Progressive Age*, xxv., 469, as practised in a place in South Wales, where it is claimed they use only 5 per cent. tar instead of 8 or 10 per cent. pitch—a most doubtful assertion! No account of the *quality* of the patent fuel obtained in this way is given.

Coal-tar is used for cementing pulverulent substances to form solid blocks by Cl. Dörr & Co. (Ger. P. 137567). The substances, sawdust, sand, pebbles, are added to the tar, heated up to 150° C., and the mixture is further heated to 150° to 200°, until from 7 to 10 per cent. of the tar has distilled off. We come back to this when treating of the employment of tar in road-making. Similar methods are contained in Rubitschung's Ger. P. 144457, and in several others which will be more appropriately treated in Chapter VI.

Mathies & Co. obtained a Ger. P. 163002 for improving coal-tar as a cementing substance by the addition of micaceous iron ore and "mineral-oil varnish."

Eiseler (Ger. P. 59244) combines coal-tar with bone-charcoal and fibrous matters under pressure to form a cement for making joints.

The "basic lining" in the Thomas and Gilchrist steel-making process is also made by the help of coal-tar.

According to Ger. P. 48701, it can be used in preparing the sand for moulds in casting iron.

Daischner (Ger. P. appl. D11210) and Culmer (Ger. P. appl. C8303) applied for German patents for the use of tar as a cement in the construction of furnaces for sodium carbonate and sulphate—an application which has been known and practised for many years.

Coal-tar used for Making and Improving Roads.

Of recent years coal-tar has very largely come into use, both for manufacturing various descriptions of "asphalt," from which

roads are constructed, or on ordinary roads, for improving these and especially for keeping them free from dust.

For this purpose both raw tar is used, and such as has been "prepared" by dehydration and in other ways which will be described later on. This has been done for many years past in France and in the United States (according to Pennock, in 1903, 16,000 tons of tar were used for this purpose in the United States), and recently it is coming more and more into use in the United Kingdom, in Germany, and in other countries. Burschell[1] gives a detailed paper on this subject. Apart from former trials in this direction, this matter was seriously taken in hand in the South of France by Guglielminetti and Schottelius. At Monte Carlo a very good result was attained, at no higher cost than by the old system.[2] Burschell attained similar results. The road looked like half-asphalted; the surface was smoother, the noise was greatly diminished. In Würtemberg, also, Braun attained very good results. There they employ as a first preparation a "thin light tar-oil," spreading it with watering-cans and brushes. The macadamized road should be as dry as possible; the oil then penetrates $1\frac{1}{2}$ to 3 ins. downwards, and about 3 lb. of it is used for each 10 sup. ft. Now the tar is put on, beginning from the central part of the road; it is heated up to 70° to 90° C., spread uniformly, and brushed in. For each 10 sup. ft., 4 to 5 lb. tar of sp. gr. 1·2 is used, when the road had not been oiled; in the other case only about 3 lb. This process is also very useful for the side-walks. In any case the roads must then be covered with sieved road-dust, and it is all the better if the process is repeated. Braun's process costs 3d. per 10 sup. ft., if 3 lb. oil at 1d. and 3 lb. tar at $\frac{1}{2}$d. have been used. According to Burschell, this is less than the cost of the ordinary road-metal, consisting of granite smalls. The tar penetrates $\frac{1}{2}$ to 1 in., and produces a tough, elastic, waterproof service.

Brix[3] reports very favourably on the success obtained by tarring roads. He recommends heatable spreading-cars. The quantity used should be $\frac{1}{3}$ gall. per 10 sup. ft. The roads should be dry during the tarring, and the weather should keep dry immediately after it.

[1] *J. Gasbeleucht.*, 1905, 1033. [2] *Ibid.*, 1903, 868, and 1904, 801.
[3] *Ibid.*, 1904, 801.

Mallet and Payet[1] report similarly about this process as used in France. They recommend an addition of 3 to 6 per cent. heavy oils to the raw tar.

Raw tar is decidedly inferior to "prepared tar" for this purpose, as proved by comparative trials in the city of Cologne.[2]

Stringfellow (B. P.) 736, 1894, mixes 100 tar with 100 water 1 alkali and 10 petroleum, thus obtaining a light red oil, then soft pitch, which can be used in shipbuilding, and an aqueous liquid. When mixing the whole before separation with dry lime and clay, an asphalt is obtained, which can be used for paving.

To be sure, objections have been raised on various sides against the tarring of roads, more especially against "surface-tarring." It is contended that the trees and other plants in the neighbourhood of tarred roads are gradually killed, that the eyes of the people on such roads are injuriously affected, and that even the durability of tarred roads against heavy traffic, motor cars, etc., is less than that of ordinary stone or macadamised roads. The reports on these points are very contradictory, but the complaints made seem to apply much less to "inside tarring"—*i.e.*, the employment of proper tar-macadam or artificial stones like that to be now described.

Much attention has been given in Germany to an artificial stone for road-making, patented by Klemens Dörr, of Germershausen u. Rh. (cf. *supra*, p. 288), and known as *doerrite*. Although this is generally manufactured by means of "prepared tar," *i.e.*, such as has been heated up to 140° to 160°, as we shall see hereafter, we will give its description in this connection. The tar is mixed with assorted gravel, previously dried, in heated drums; the mixture is moulded by means of a pressure of 4 atm. into plates or bricks which are cooled by water on the carrier band. They consist of 17 to 20 per cent. tar and 83 to 80 per cent. silica. At the time of that report they were produced at a rate of 4000 tons per annum. The plates have a rough surface, and therefore are very well adapted not merely for side walks, but also for stables; they are quite water-tight, and form a warm flooring. At Stuttgart the same material is used for jointless roads. For this purpose it is put on in a warm state, rammed in, and rolled after three or four days. In that city

[1] *J. Gasbeleucht.*, 1904, 945. [2] *Asph. u. Teer-Ind. Zeit.*, 1905, 20.

they employ basalt smalls and prepared tar, and give the plates a thickness of 4 ins.; the cost is 5s. per 10 sup. ft. They claim for it the following advantages: freedom from noise, avoidance of slipping, resistance against water and alkaline liquids, and inconsiderable wear and tear.

Powell, in 1905,[1] gives a favourable report on this process as carried out in England. The cost of the whole apparatus was £400. The daily output of 35 tons mixture required 1¼ ton coal-tar, 4 cwt. pitch, 5 cwt. coke, and 4s. 2½d. total cost per ton of gravel, inclusive of interest and depreciation. While before this the roads had to be repaired every three years, they now stand seven or eight years up to ten years, and are entirely free from dust and dirt.

Many similar reports have been made during these last years on tar-pavements in various parts of Germany. In France a special Société de Goudronnage des Routes has been established (17 rue de Bourgogne, Paris), which extends this process more and more every year.

Asphalt and Pitch from Tar without distilling it.

As far as such substances are made from products obtained in the distillation of tar as residue in the stills, we shall treat of them in Chapter VI. Here we only treat of such processes as are employed for converting raw tar into solid or semi-solid substances of a prevailingly organic character, similar to asphalt and pitch.

Peck (Ger. P. 124629) makes artificial asphalt by mixing 50 parts tar, 50 rosin, 50 petroleum residues, heating to 160° C., and then slowly up to 177°, and adding 3 to 6 parts brimstone.

Trainer (Ger. P. 134100) heats wood, coal, etc., with tar under pressure, and thus obtains a kind of pitch. An addition was applied for as T7826, Class XXII.

Jasset (Fr. P. 327959) prepares a substitute for indiarubber by heating 100 coal-tar with 25 boric acid, burning off, and passing oxygen through the mixture.

Coulson (B. P. 2102, 1904) prepared a solidified tar by heating tar with sulphuric acid. He employs raw tar, while Wirkner employs the same process for heavy tar-oils (*cf.* next page).

[1] *J. Gas Lighting*, No. 2207, p. 554.

Wendriner (Ger. P. 170932) also heats tar or tar-oils with sulphuric acid, but he adds to this a treatment with hot steam up to the point where the sulphonic compounds are hydrolyzed, and a residue is obtained, practically free from sulphur, neutral and insoluble in water. This is mixed by fusion with the hydrocarbons driven off by the steaming, in order to obtain a product of the desired degree of viscosity.

Sulphuric acid is also employed by G. von Wirkner (B. P. 13185, 1903; Ger. P. 158731). He heats tar or tar-oils with from 10 to 100 per cent. sulphuric acid of sp. gr. 1·71 to 180° C. or above, until the sulphuric acid is decomposed, and the volatile substances have distilled off to a sufficient extent so that the remaining pitch has the intended degree of hardness. If more sulphuric acid be used, substances are formed which have no more the character of pitch, or the carbonization goes too far.

Frances Merrill (Ger. P. 160617) heats the 85 coal-tar with 10 per cent. water and 5 per cent. ferrous sulphate to 300°. Thus pitch is obtained which is brittle, easily reduced to powder, and easy to mix with the small coal for briquettes, without the trouble caused by the employment of sulphuric acid through the escape of acrid gases.

The Société anon. des Combustibles industriels at Haine St Paul (B. P. 16182, 1905; Ger. P. 161950) make pitch from tar by treating it with ozone or chlorine peroxide in the presence of alkalis, lime, or dolomite.

The Chemische Fabrik Flörsheim, Dr Nördlinger (Ger. P. 171380), employs the oxidising action of air. He had previously applied this to getting pitch-like substances from wood-tar (Ger. P. 163446), and he now extends this to coal-tar and tar-oils. His process consists in heating the tar to about 120° to 150° C. in the presence of air, oxygen, or ozonised air, until the product shows the desired properties.

Trillich (Ger. P. 200524) stirs 12 parts of dried and sifted spent gas-lime into 100 parts of dehydrated tar, and thus obtains an asphaltum-like pitch easily soluble in benzol.

Rudolph Rütgers had already, in 1904 (B. P. 23680, 1904), described a process for the manufacture of pitch from heavy tar-oils by introducing heated air into the hot tar-oils. Later on (B. P. 3192, 1906) he shows that this process may be applied to the tar itself by heating it directly while air, or other gases

containing oxygen, or ozonised air are introduced into it. The first heating of the coal-tar drives out the light oils, carbolic acid, and pyridines; later on the intermediate oils are driven out with naphthalene, and at last the residue is converted into pitch. The process may be accelerated by the presence of catalytic bodies, such as copper salts. When applying the air for six hours at 220° C., a more viscous and less odorous product is obtained. By continuing the heating, intermediate products, and at length brittle hard pitch may be obtained. The process differs from known processes by producing a maximum of pitch, through limiting the distillation and regulating the temperature in such manner that as much as possible remains in the retort, where it is converted into pitch by the action of hot air. In the ordinary distillation of coal-tar only that pitch is obtained which forms part of the raw tar; but by this process the distillable portion of the tar is also to a great extent converted into pitch.

Solidified Tar.

The Tar Patent Solidifying and Distilling Co., according to *Chem. Trade J.*, 1907, xl., 191, distil off the water and crude naphtha, and run the residue, while hot, into a vessel, where it is mixed with 5 per cent. of a material (such as granite chippings), which causes it to solidify, and thereby renders it more portable. The solidified blocks may be used for all the ordinary purposes of gas-tar, or of pitch in the manufacture of briquettes, and the light oils are still obtained from the material as in the ordinary process of tar-distillation.

Coal-tar and Preparations from it for Antiseptic and Medicinal Purposes.

The antiseptic property of coal-tar has for a long time been known and utilized; its action as a paint on wood depends partly upon this. No doubt it results from the fact that tar kills the lower organisms. For this reason it has also been tried against the potato- and grape-disease; but in these cases the cure may be worse than the evil. Vines treated with coal-tar or the heavy tar-oils mostly yield objectionably flavoured

BIRMINGHAM REFERENCE LIBRARY PUBLIC LIBRARIES

grapes, and the wine made therefrom is affected in a similar manner.[1]

E. Koch has patented a mixture of tar with gypsum, sand, lime, silica, or aluminium silicates, as an insecticide manure, and for preserving corn, other seeds, and the roots of vines from the ravages of insects (Ger. Ps. 14616 and 18637).

Coal-tar is also used for painting the wooden floors of hospitals, barracks, workmen's dwellings, etc., in order to render them water-tight, and to diminish the danger from germ-infection. One kg. of coal-tar suffices for a surface of 10 sq. m. = 107 sq. ft.[2]

Tar, or mixtures containing it, is frequently used for disinfecting cesspools, sewers, etc. The best-known in England is MacDougal's disinfecting-powder (consisting of 100 slaked lime, 10 coal-tar, 15 magnesium chloride); in Germany, Süvern's disinfecting-mixture (100 slaked lime, 15 coal-tar, 15 magnesium chloride). No doubt raw tar is inferior in this respect to the specifically disinfecting-substances it contains, such as phenol and naphthalene.

According to Sack (*Chem. Zeit.*, 1903, Rep., p. 148), the Chemische Fabrik Knoll & Co., of Ludwigshafen, sells a "purified tar," entirely free from free carbon, in appearance like olive oil, for medicinal purposes; it is stated to be specially adapted for the treatment of skin diseases, on account of the absence of pitch. The product is called "Anthrisol."

Joseph Giraud deodorizes tar or tar-oils for the manufacture of soap, etc., by heating with ammoniacal copper solution or by salts of iron, manganese, or chromium, adding an alkali and passing steam through the mixture.

Tixier (Ger. P. 138764, 1901) obtains all the soluble "extractive substances" contained in tar in a single operation as follows. A mixture of tar and sodium carbonate, corresponding to its percentage of soluble substances, is heated at a temperature between 60° and 100° C. The quantity of Na_2CO_3, as well as the most suitable temperature, is ascertained by previous trials. The mass gets into a state of frothing, the end of which

[1] Cornu (*Comptes rend.*, 2nd October 1882). Watson Smith (priv. comm.) has met with a similar objection in the case of celery grown by the aid of manure made from vitriol-tar and lime.

[2] *Gesundheits-Ingenieur*, 1886, p. 434.

shows that the reaction is over. Now a quantity of cold water, sufficient for dissolving the soluble portions is added and the solution decanted. By means of an acid the substances are precipitated, and mixed in the necessary quantity of sodium carbonate at 60° to 100° C. This produces a pasty extract, soluble in water, which can be brought into a solid form or into solution in the usual manner, and is used for antiseptic purposes in medicine.

Mann (Ger. P. 170133) dissolves such substances in a suitable volatile solvent, and pours that solution into a mixture containing both soap and some organic or inorganic colloid substance, *e.g.* starch. This mixture is heated and thoroughly stirred up, *e.g.*, by means of a steam-jet. When running the solution, say, of asphalt in benzol, into the hot mixture, the benzol volatilizes and is recovered by condensation ; the asphalt, etc., remains behind, intimately mixed with the liquid, and remains in this state, if the agitation continues until the mass has cooled down. If necessary, more water is added during this process, always with energetic oxidation. In this way an emulsion is obtained like an unguent, which mixes quite uniformly with water and forms a durable emulsion.

Coal-tar for Denaturing Alcohol.

Hacke (Ger. P. 144485) mixes decanted tar with its own volume of spirits of wine, separates the liquid from the sediment, dissolves it in 1 to 10 parts benzol, and employs 1 part of it for 100 spirit of wine.

The Manufacture of Lampblack and Soot.

Formerly lampblack, which is the most important raw material for printers' ink and for many black paints, had to be made by burning rosin or rosinous wood. The introduction of coal-tar has completely revolutionized this manufacture.

Raw tar is not very well adapted for it, owing to the presence of water and volatile substances, which make the soot impure and sometimes yield explosive mixtures. Therefore, just as in the manufacture of roofing-felt, the tar is deprived of those substances by partial distillation; or else "prepared tar," creosote oil, or pitch are employed. The coarsest quality of

soot is obtained from pitch; then follow "prepared tar," partly distilled tar, and best of all creosote oil. Lampblack proper is always made from gaseous raw material.

Tar is burned for soot in brick furnaces, connected with long brick flues, where the smoke-gases can deposit the flakes of soot before escaping into the air. Engler describes this industry as carried on in the Black Forest, where about 250 tons per annum are made in the following way:—

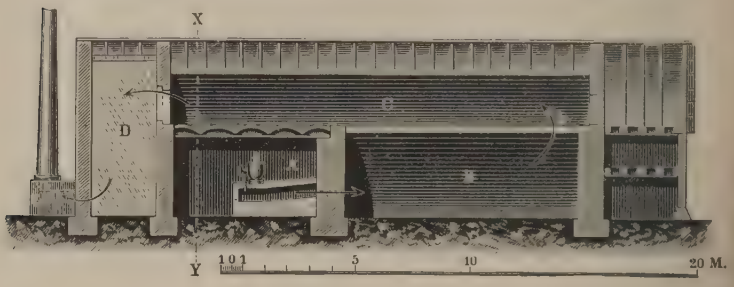


FIG. 68.

FIG. 69.

Figs. 68 and 69 show the furnaces A, into which solid pitch, etc., is charged by hand; tar or oils are run in by pipes from the vessels *a*. The smoke travels first into the cooling-vault B, then through *b* into the long vault C, then into the tower D, divided into two compartments by a perpendicular partition, and through a damper into the chimney. The last portions of soot are retained by a coarse fabric extended across one-half of the tower. The work is commenced on Tuesday, is daily interrupted from 9 P.M. till 5 A.M., and continued till Saturday. On Monday the chambers are emptied.

These furnaces do not provide for cooling the flame, which is, however, preferable for obtaining a better yield of soot. An improved furnace (according to Köhler) is shown in Figs. 70 and 71. *a* is a cast-iron fire-plate, angularly shaped, so that the liquid fuel cannot run out in front; *b* is a conical cooler of ¼-inch sheet-iron, with a tight-fitting cover, manhole *f*, steam-pipe *g*, gauge-cock *e*, and running-off tap *q*. The liquid fuel is supplied through the 2½-inch pipe *d*, from the heater *n* to the fireplace *p*, and runs out of small bent pipes regulated by a tap. These small pipes can be turned sideways in their sockets, when solid fuel (pitch) is to be charged by hand. The fireplaces *p* are

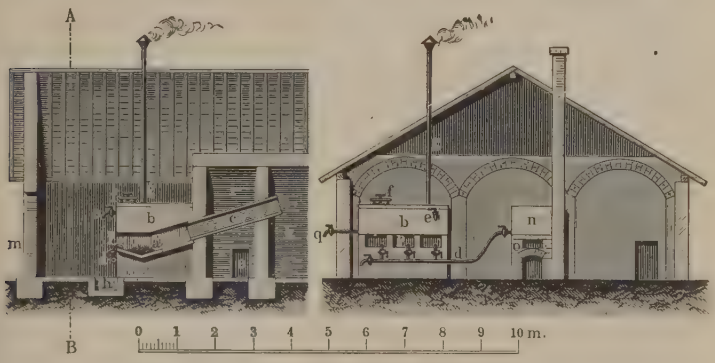


FIG. 70.

FIG. 71.

provided with a slide-door, adjustable in any position by toothed gear; *c* is a square flue made of sheet-iron 12 ft. long, for conveying the gases through the cooler *i* into the chambers *k*; *h* is a channel, kept full of water by means of a tap, to extinguish the coke falling out of the fire and removable by the door *m*.

The chambers *k* consist of three parallel vaults, each about 120 feet long, through which the smoke-gases travel in succession before escaping through the 50-ft. chimney. These vaults are provided with a number of inside partitions, causing the gases to travel consecutively along the bottom or top of the chamber. All the compartments thus formed are connected by iron doors one with another, and at the end opposite the fire with a common collecting and packing room.

To begin with, a good fire is made on the fire-plate *a* by means of paper, tarred or oily cotton-waste, etc., and then the proper fuel is supplied in the approved way. Every day about 15 cwt. of tar or pitch can be burned, the work being carried on as described in the Black Forest. All doors leading outside must be kept tight by pasting paper over the joints, as a precise regulation of the draught is very important to obtain a good yield, which should be 25 per cent. from tar and 18 to 20 per cent. from pitch.

This arrangement permits of utilizing the heat of the fire for evaporating large quantities of liquid, as is easily understood.

The following description of lampblack-making has been given by Nepp.[1] The tar is employed for heating six steam-boilers 13 ft. long, 2 ft. 2 ins. in diameter, which jointly supply an 8 h.p. steam-engine. The tar is run into tanks holding two barrels each, one in front of each boiler. Behind the boiler is an oven, in which the gases from the burning tar, which have been partially cooled in their course through the boiler-flues, deposit the soot contained in them upon horizontal and vertical shelves, which divide the oven into several compartments. The lightest particles of soot are deposited in the highest part of the oven; and this does not require to be so often emptied as the middle and lower shelves, which contain most of the lampblack, and are emptied directly after the tar has been burnt off. The work lasts six hours and proceeds by turns, three ovens continually going together, so that there is always enough steam. In the fireplace a residue of fine coke is found. The ovens are well bound and covered with metal plates. They are 13 ft. high; the upper 3 ft. project through the roof, so that they are cooled from without. They are accessible from below by an iron door, from above by iron steps. The lampblack is partly left as it is; but most of it is mixed with peat, finely ground under edge-rollers, and sifted before it is sent out. The steam generated in the boilers is employed for driving a peat-mill, manufacturing the casks, etc. The cost of plant is about £400 to £450. The product serves for manufacturing colours, shoe-blacking, black-lead for stoves, etc.

Thenius[2] describes several lampblack-furnaces of a very

[1] *Chem. Zeit.*, 1878, p. 222.

[2] *Die technische Verwendung des Steinkohlentheers*, p. 132.

simple kind, intended for burning tar-oils, pitch, etc. The furnace for "soot-oil" consists of a metal plate kept red-hot from below by a local small fire; it forms the bottom of a brick chamber. Upon this the "soot-oil" constantly drops in a fine stream from a tank, whilst a side door with small holes admits the air necessary for combustion. The smoke enters four brick chambers, communicating with a chimney. When the oil intended for combustion has been used up, the furnace is left standing for a few days, and the four chambers are opened by doors provided for the purpose. The last chamber (next to the chimney) contains the finest lampblack (for lithographers); the third one the next finest (for printers); the second and first contain coarser soot, which is well sifted and sold as common lampblack. The best kind is sometimes further refined (for paper-makers, colour-manufacturers, lithographers) by ignition in sheet-iron cases, the covers of which are luted with clay. They must be heated for some time in a furnace with a good draught, till all empyreumatic oils have been driven off and the soot remains behind without any smell. The cases must be left to cool for several days before opening them, because the soot cools very slowly and would take fire if it were exposed to the air too soon. This is "half-calcined lampblack"; the "thoroughly calcined" article is obtained by igniting the first product once more in fresh cases and treating it as above. Four hundred pounds of "soot-oil" (*i.e.*, heavy coal-tar oil) should yield 20 lb. finest lampblack, 30 lb. seconds, and 23 lb. of the third and fourth qualities. On the metal plates some coke remains, which is knocked off and sold as fuel.

The English plan of calcining soot consists in putting a small portion into a circular iron pan, about $2\frac{1}{4}$ ft. high and $2\frac{1}{4}$ ft. in diameter, lighting it by a red-hot iron, and adding more from time to time as the ignition proceeds. When the pan, being full, ceases smoking, the cover is put on and its contents are allowed to cool. There is about 25 per cent. loss in this process, which should be conducted in a well-ventilated, closed building.

J. Bronner[1] burns all waste products of tar-distilling under a specially constructed steam-boiler of somewhat complicated construction, and forces the products of combustion by means

[1] Private communication.

of a fan-blast of 7 ft. diameter through long flues, provided with ground-in bottom-slides, into a soot chamber. The slides serve to admit air as well, in order to make different qualities of soot, according to their position, for all technical purposes—such as "fat soot" for oil-cloth manufacturers, and calcined soot of all kinds for patent leather, indiarubber, and printers' ink manufacturers.

The smoke issuing from the chimney of lampblack chambers is rather offensive; this should be avoided by making the passage of the gases so long that at last all the soot is effectually condensed. In an English works there is a "black-house," 150 ft. long, and so divided by partitions as to cause the smoke to traverse a distance of 500 ft.; it then passes through a fire in which it is completely consumed.

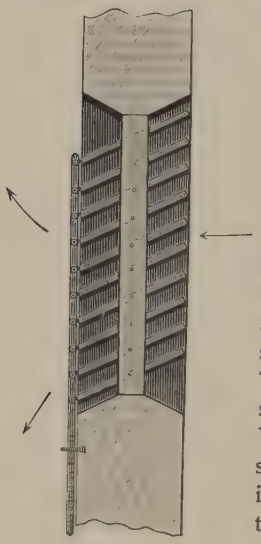


FIG. 72.

The last portions of soot, before the gases issue into the air, are usually retained by coarse canvas, or by a wire sieve; but these filters are quickly stopped up and cause much trouble. This is avoided by Köhler's apparatus, shown in Fig. 72. It is a kind of Venetian blind, 3 ft. square, made of sheet-iron; the flakes of soot, on striking against this, are deflected and fall to the bottom, whilst the gases pass out without hindrance.

The same object is more completely attained by Siemens's "spiral deflector," Fig. 73, where the gyrating movement imparted to the gases causes the solid particles to coalesce into larger masses, which, on leaving the spiral in a tangential direction, strike against the walls of a collecting-chamber, whilst the gases escape into the chimney.

Other arrangements for the same purpose have been described by Lindner (Ger. P. 47907), Benoist & Camolly (Fr. P. 226418), Dewey (Ger. P. 51896, B. P. 14644, 1889), Goulard (Ger. P. 34324), Wassermann (Ger. P. 35104), Rössler & Reinhard (Ger. P. 54201), Schlösser & Ernst (Ger. Ps. 31108

and 35942), Rösing (Amer. P. 432410), Neuninger (Ger. P. 56742), Eichfelder & Winckelmann (Ger. P. 57278), Schneider (Amer. P. 487971), Mueller (Amer. P. 492255), Wegelin (Ger. Ps. 179179, 198646, 201262, 202118), Meiser (Ger. P. 203711).

The observation made by Prof. Lodge, that soot or similarly

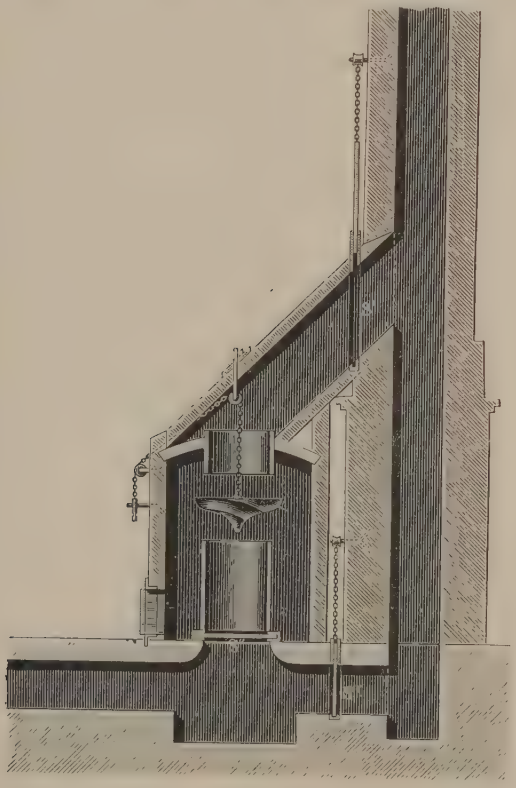


FIG. 73.

finely suspended particles may be caused to subside rapidly by means of an electric current, has been followed up by Irvine and Mitchell,[1] and with perfect success, but the cost of the process has so far prohibited its practical application.

[1] *J. Soc. Chem. Ind.*, 1889, p. 377.

Thalwitzer (Ger. Ps. 9426 and 13691) prepares lampblack by rotating metal disks, cooled with water, over lamps fed with oil, and removing the soot formed by scrapers.

The soot, as it is removed from the chambers, is directly fit for most uses. Enormous quantities are now consumed in the manufacture of carbon electrodes; also in that of patent leather and for printers' inks. In this crude state soot contains tarry substances, which can be easily perceived by rubbing it up with a few drops of spirit of wine or benzol on a piece of white paper, when a brown colour will be noticed on the other side of the paper.

For better printers' and lithographers' ink these empyreumatic substances must be removed, which is done by *calcining* in closed pans in a furnace, as shown in Fig. 74, about 5 × 5 ft. wide and 12 ft. high. At the bottom there is a grate (C), provided with an ash-pan (B). Above C five brick arches (D) leave spaces (E) of 4 ins. width for the passage of the fire-gases. The space above the arches is levelled by brickwork, so that twenty-four rows of cast-iron pots can be placed on it, 9 ins. wide, 16 ins. high, and $\frac{1}{4}$ to $\frac{3}{8}$ in. deep. Each pot is provided with a rebate round the top, into which fits the bottom of the next higher pot, only the top pot of each row having to receive a separate cover. The joints are well luted with clay. The charging-door K is bricked up during the operation. The fire-gases escape through four flues (F, F) in the four corners into a common chimney (I). The furnace is fired for 18 to 24 hours till red-hot, and must then be allowed to cool down completely, as the hot calcined soot would take fire in contact with air. It forms a light, coherent mass, which is sold either as such or in the ground state.

The colouring-power of soot is all the greater the more it has been purified from tarry matters. Runge[1] examines it by mixing 1 part of soot with 2 of alcohol and 24 of gum-water (made from 2 parts of gum-arabic), taking up some of the mixture with a dry brush, weighing the brush along with the paint, and painting with it on writing-paper divided into squares. The colouring-properties of the soot correspond to the weight of the paint used and the number of the blackened squares.

[1] *Grundriss der Chemie*, 1842, i., p. 65, on the authority of Schultz, *Steinkohlentheer*, 2nd ed., vol. i., p. 91.

Wilhelm and Bohnstadt (Ger. Ps. 12282 and 12286) make *printers' ink* by mixing 100 parts of coal-tar with 6 to 15 rosin and 10 paraffin oil, forcing through a sieve, treating with bleaching-powder to destroy the smell, and mixing with 20 to 25 parts of glycerin and 12 to 18 parts of lampblack; for the

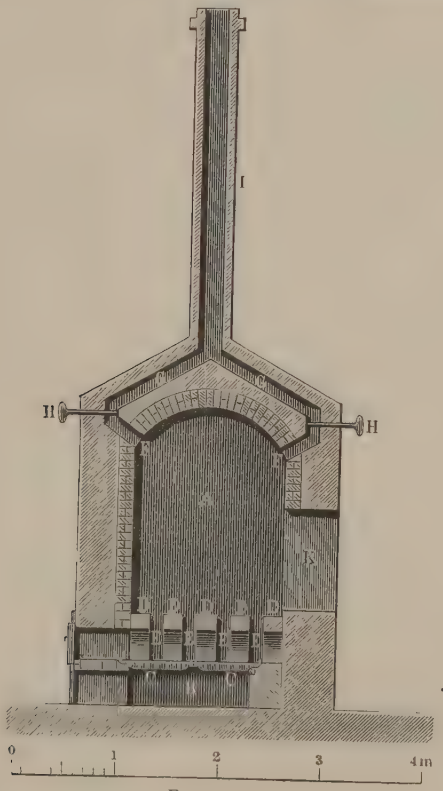


FIG. 74.

finer qualities a dark aniline colour is added. Or the tar is first heated with $2\frac{1}{2}$ or 3 per cent. sulphuric acid, neutralized with soda, treated with chlorine as above, mixed with $2\frac{1}{2}$ or 3 parts of lard and 4 or 5 parts of glycerin or 8 to 10 parts of soap. Sometimes they add $\frac{1}{10}$ to $\frac{2}{10}$ per cent. lampblack and logwood extract with bichromate of potash, alum, or cream of tartar.

According to Newton's patent of 1854, lampblack can be obtained directly by mixing 160 lb. of coal-tar with 200 lb. of slaked lime, adding 18 lb. of alum, and strongly heating the well-kneaded mixture without access of air in fireclay crucibles or iron cylinders, as in preparing bone-charcoal. The product should be allowed to cool down without access of air, and is at last finely ground. By altering the proportions of tar and lime, all shades between brown and grey can be obtained.

Of recent patents on the manufacture of soot from coal-tar, we mention the following :—

Wegelin (Ger. Ps. 129647 and 138940; B. P. 13837, 1903) heats the tar to boiling and burns the vapour, by injecting the previously heated air into the boiling tar, thus obtaining pitch as a by-product. An additional patent (Ger. P. 179179) protects the utilization of the radiant heat of the mixture of gas and air, and the agitation of the boiling tar by injecting carbonic acid or steam or by mechanical stirring, for the purpose of preventing the superficial formation of slag and coke.

The Kölner Russfabriken (Ger. P. 133270) burn the tar incompletely without previous distillation, obtaining pitch as a by-product.

Irvine (*Chem. Zeit.*, 1902, Rep., p. 80) causes the soot to precipitate more quickly by means of the electric current.

Hartmann (Ger. P., Anm. H26230) aims at increasing the density of the soot.

Ogilvie obtained a German patent (No. 148258), which lapsed already in 1904, for directing the flame of tar immediately on the surface of water.

A long paper on the manufacture of soot has been published by Luhmann in *Asph. u. Teer-Ind. Zeit.*, 1903, pp. 511, 530, 545.

Maechtolf (*Z. angew. Chem.*, 1908, p. 1088) has taken two German patents for the manufacture of lampblack. According to the first, No. 194301, of 1905, he employs a decomposing cylinder, in which he produces lampblack from hydrocarbons by means of the electric arc, or by fulminating mercury. This cylinder is provided with an agitator and is connected with a soot-collector, in which a press-piston moves up and down and to which is attached an arrangement for packing the barrels. According to his second patent, No. 194939, of 1905, lampblack of specially good quality is obtained by pre-heating the

hydrocarbons to be decomposed, and at the same time subjecting them to variable pressure; also by mixing them with hydrocarbons decomposed at lower temperatures (such as acetylene), first in larger, then in smaller quantities, until the temperature has risen to such a height that the heavy hydrocarbons are decomposed without admixture.

Of new applications of the soot produced from tar, we mention the following:—

Meurer (Ger. P. 133502) employs it for staining glass with a red colour. In order to prevent the loss of the soot in the glass crucible in the shape of dust, he previously mixes it with sugar syrup and moulds it by compression.

The formation of soot from tar has been utilized for protecting vineyards during cold nights against the action of frost (Russig, *Chem. Zeit.*, ii., p. 238).

Coke from Tar.

Dahmen and Haggi Ristic (B. P. 20967, 1903) introduce tar in a thin jet into white-hot iron retorts, where it is decomposed with deposition of coke.

CHAPTER V

THE FIRST DISTILLATION OF COAL-TAR

Historical Notes.

IT has been mentioned more than once in the preceding chapters that the utilization of tar by distillation is a comparatively new industry; but it had long been known that useful products could be obtained by that operation. In this respect a patent awarded to Henry Haskins, 7th August 1746 (*i.e.*, half a century before the first introduction of gas-lighting), is so remarkable that I quote it verbatim, as follows:—

"New method of extracting a spirit or oil out of tar, and by the same process produce the finest of pitch.

"First, take any quantity of tar you please, so as not to more than half fill your still, which must be thoroughly cleaned from all manner of impurities, and more particularly from water; for if any quantity of that should be left in it, it will be found to be exceedingly troublesome and considerably hinder the operation.

"The tar may be cleansed either by boiling or straining, or by settling in tubs, or any other convenient vessel; then commit it to a double-necked pelican-headed still, made either of glass, iron, or copper, with capacious receivers, and well luted, under which raise a fire of the first degree for six hours, by which time the particles will be thoroughly comminuted; then raise your fire to the second degree for as many hours more, and then to the third degree for three hours more, in which time you will find first a pale acid phlegm to come off into the receiver, which must be changed, when a fetid volatile oil or spirit rises; lastly will come over a black glutinous oil, which keep for use.

"If you would have a more volatile or light oil, which may

be more proper for many uses in physic, it may be done by many repeated rectifications to what degree you choose.

"Lastly, the caput mortuum, which is what remains in the still after the distillation is finished, will be found the finest and best of pitch, which I am well assured of, not only from my own judgment, but by the experience and testimony of many who have used it."

It is quite possible that in this patent wood-tar is meant, which at that time was much better known than coal-tar; but the principles of the distillation of the latter appear quite clearly in that old patent.

We have seen (on p. 9) that Accum, in 1815, was the first to boil down coal-tar in closed vessels (stills), and thus to obtain a volatile oil which could be employed as a cheap substitute for spirits of turpentine.

According to Dr Longstaffe,[1] the first coal-tar distillery was erected by himself and Dr Dalston, near Leith, in 1822; the spirits went to Mr Mackintosh for waterproofing, and the residue was consumed for the purpose of making lampblack.

Roscoe[2] mentions that, about the year 1834, at the time when Mitscherlich had converted benzene (from benzoid acid) into nitrobenzene, the distillation of coal-tar was carried out on a large scale in the neighbourhood of Manchester; the naphtha obtained was employed for the purpose of dissolving the residual pitch, and thus getting black varnish. Attempts were made to supplant the naphtha obtained from wood-tar, which at that time was much used in the hat factories at Gorton, near Manchester, for the preparation of "lacquer," by coal-tar naphtha. The substitute, however, did not answer, as the impure naphtha left on evaporation so unpleasant a smell that the workmen refused to employ it. It was also known, about the year 1838, that wood-naphtha contained oxygen, whilst that from coal-tar did not; and hence Mr John Dale attempted to convert the latter into the former, or into some similar substance. When trying, for his purpose, a mixture of sulphuric acid and potassium nitrate, he obtained a liquid possessing the smell of bitter-almond oil, the properties of which he did not further investigate. This

[1] *Proc. Soc. Chem. Ind.*, 1881, p. 13.

[2] Discourse at the Royal Institution, 16th April 1886, p. 4.

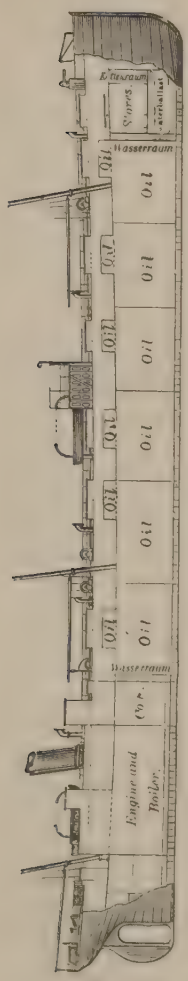


Fig. 76.

Fig. 75.

was, however, done in 1842 by Mr John Leigh, who exhibited considerable quantities of benzene, nitrobenzene, and dinitrobenzene to the Chemical Section of the British Association, meeting that year in Manchester. His communication is, however, so printed in the Report that it is not possible, from the description, to identify the bodies in question; and hence Leigh's merits in that respect were completely overlooked until quite recently.

The further steps in distilling coal-tar and utilizing the products therefrom, made by Bethell, Brönner, and Mansfield, have already been noticed (pp. 9 *et seq.* and pp. 177 *et seq.*), and from that time dates the establishment of tar-distilling on a really large scale.

Carriage and Storage of Coal-tar.

Various descriptions of vessels are used for carrying the tar from the gas-works to the distilleries, according to the circumstances of the case. In England water-carriage is preferred whenever it is practicable, the canal-boats being constructed as floating tanks, with a cabin for the crew, which serves also as an air-space for augmenting the carrying-power. Such boats (Figs. 75 and 76) hold as much as 10,000 galls., or about 50 tons of tar. On the Continent this is rarely possible; there the tar is usually carried by railway, in cylindrical or angular iron tanks fixed on a platform running on wheels (Figs. 77 and 78). If these tanks are made of pretty strong iron, they can be steamed out whenever the tar has become too thick, which may happen in winter. In Germany they are frequently provided with heating-

tubes, connected with the steam-heating system of the railway train. Angular (box-shaped) receivers are more easily got at and cleaned inside; they hold about 10 to 15 tons, a truck with

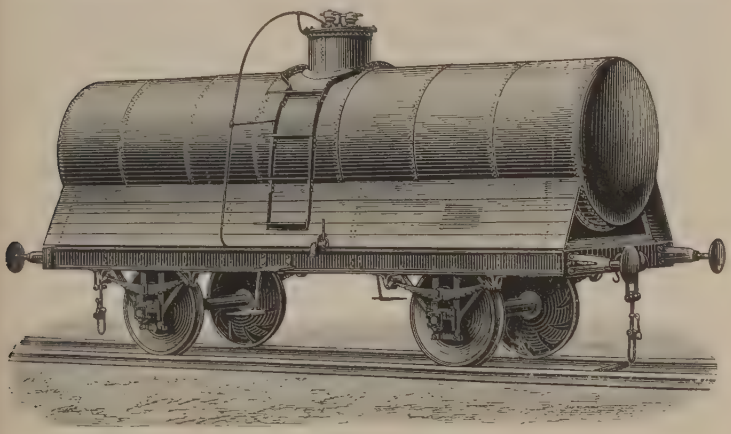


FIG. 77.

two cylinders about 9 tons of tar. It is convenient if they are provided at the top with a pretty large pan serving in filling the tank, and with a movable crane for lifting up the full casks and lowering the empties.

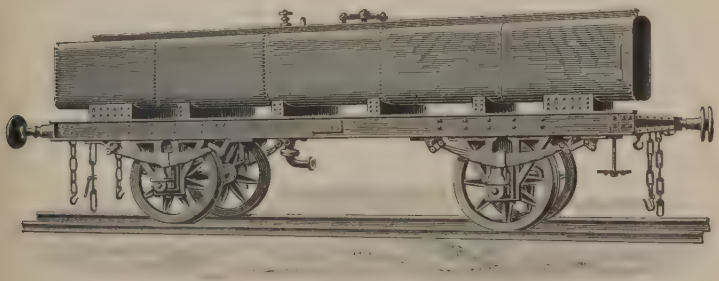


FIG. 78.

Tar-barges or tank-waggons ought to be air-tight, so as to obviate the escape of effluvia (principally sulphide of ammonium) during the transit. While pumping, the cover should only be opened just sufficient for the pipe to pass in.

In Paris (and elsewhere) tar is carried in iron or wooden casks resting on axles and drawn by horses, or, wherever possible, laid on railway-trucks. In Lancashire[1] it is usual to employ wooden barrels (preferably of ash-wood), holding from 250 to 300 gall., resting by means of concave wooden bearers upon two-wheeled carts. The middle bearer rests just over the axle; and the barrel can be tipped behind, two iron adjustments attached to the back bearer preventing it from slipping down. There is a running-off cock of 2- or 2½-in. bore, and a charging-hole 4 or 5 ins. square and closed by a wooden plug. Long barrels are said to be pulled more easily than those more bulged. A barrel costs about £3, the cart pertaining to it £14.

From the canal-boats or trucks the tar is frequently pumped by steam-pumps into iron *store-tanks*, situated high enough for the tar, after the water has separated, to be run into the stills by natural fall. In Paris the draw-off cocks of the cylindrical iron store-tanks, which rest on high pillars, unite into a common main, which descends to the ground, runs underneath along the whole set of tar-stills, and gives off an upright supply-pipe with slide-valve for each still, by which these can be filled as required, by means of hydrostatic pressure, from the store-cylinders. In other cases the tar, especially when it arrives in casks, is emptied into larger store-cisterns sunk in the ground, and pumped from these either into the above-mentioned high tanks or directly into the stills.

Such underground tar-wells (also those for ammoniacal liquor) are frequently of very large dimensions,[2] as tar-distillers are generally bound by contract to rid the gas-works of their tar and ammoniacal liquor, which in the event of stoppages of business, accidents to the plant, etc., might cause them considerable embarrassment. On the other hand, if there is large storage room, a good stock may be collected in winter, when the gas-works are busiest, so that even in summer the stills can be regularly employed (Watson Smith).

Underground wells are not often made of iron, this being too costly and subject to corrosion. Usually they are made of brickwork set in cement, of a circular shape, secured underneath and round the sides by clay puddle. First the necessary

[1] Watson Smith.

[2] Watson Smith mentions some of 60 ft. diameter.

excavation is made; then a good puddle is laid down on the bottom, completely levelled, and a double floor of bricks in cement laid on, the joints crossing each other. Now the sides are raised, likewise in double courses and hence 9 ins. thick, leaving between the brickwork and the soil (in case of need kept back by wooden stays) a space of 8 or 12 ins., which is filled in with puddled clay. The best method of proceeding is to complete each time a ring of about 4 ft. high, puddle behind it, and continue the walling. It is best not to work too fast, so that the brickwork may have time to settle; cracks once formed can hardly ever be repaired (Watson Smith).

Tanks made by the Monier system (cement concrete with a core of wire-netting) are said to be much cheaper and quite as good as brick tanks; they can be placed either below or above ground.

The tar-wells are tightly covered with planks, to keep out the rain, etc. At the place where the carts are tipped there is a strainer with many ½-in. holes and with sides and back, so that any bits of wood which might choke the pumps are kept back (Watson Smith). Or else all the carts discharge their contents into a large spout, provided with outlets for each cistern (if there are several).

The tight covering-in of the tar-cisterns also avoids any nuisance from offensive gases whilst running-in the tar. For this purpose the air driven out by the tar is made to pass through a box containing hydrated oxide of iron, which absorbs any hydrogen sulphide escaping (*cf.* later on the various plans for dealing with the noxious gases).

The *pumping of the tar into the stills* was formerly always done by ordinary pumps, specially constructed for thick liquids, and provided with a strainer at the suction-pipe to prevent choking up by chips of wood or the like. It was considered that such a thick liquid could not be raised by compressed air. This is, however, nowadays actually done at all larger German works. Previously warmed-up tar can be pumped into the stills by means of air compressed to 28 lb. per square inch in half the time as with a good ram-pump.

The pumping by compressed air is effected by placing a pressure-vessel (usually an old steam-boiler) beside and a little below the tar-reservoir, and connecting them (for large stills) by

an 8-in. pipe and valve. This vessel should hold either half or the whole contents of a still. It is connected with the still by a 5- or 6-inch wide iron pipe, rising to the same height as the level of the tar in the still when full, with a valve just outside the still. This allows of providing for the frothing-up of the tar, by reconducting the rising tar into the pressure-vessel (see below). A removable strainer is placed just before the pipe connecting the reservoir with the pressure-vessel. If, in spite of this, the valve becomes choked up, it is easily freed again by admitting compressed air from the pressure-vessel into the tar-reservoir. A pressure-vessel holding 15 or 20 tons is filled from the reservoir in ten or fifteen minutes, and, with air compressed to 28 or 35 lb. per square foot, is pumped up 15 or 16 ft. high in an hour or an hour and a half.

Distillation by Steam.

The manufacture of coal-tar products begins by fractionally distilling the tar, mostly by a naked fire, but in some places or for special purposes by means of *steam*. The latter plan is now very little used at large works—except in Scotland, where it appears to be general. Its advantage is only apparent where the tar has merely to be dehydrated and deprived of its most volatile constituents in order to employ the remainder (95 per cent.) for painting, for impregnating stones or roofing-tiles, or for the manufacture of roofing-felt (*cf.* p. 280). In such cases much trouble and danger of fire is avoided by substituting steam for a naked fire. The steam can be applied indirectly, as "dry steam," by surrounding the still with a jacket, or by means of a coil in which the steam circulates inside the vessel and issues again to the outside. In the outlet it is expedient to fix an apparatus for automatically discharging the condensed water, without allowing any steam to escape, of which apparatus many kinds are now made. The still may be of almost any shape; perhaps the best is an upright cylinder. The escaping vapours are condensed in a leaden or iron worm and separate in the receiver into ammonia-water and light oil, which is mostly sent to the larger tar-distillers for rectification.

It is more usual to employ "wet" steam, directly blown into

the still, *e.g.*, by means of a coil of pipes lying on the bottom and perforated with many holes. According to Ure, such stills hold from 800 to 1500 galls., and the distillation is carried on till the specific gravity of the distillate has reached 0·910. According to Mills,[1] the stills hold from 500 to 4000 galls., and are horizontal cylinders; the steam brings over about 10 per cent. at most of light naphtha (sp. gr. 0·78 to 0·83) and some ammoniacal liquor. The residue is run into cisterns, where, on its settling, tar and water separate. The "boiled tar" is now ready for the above-mentioned purposes, or can be run while hot into other stills for distilling by naked fire, which is the usual course followed in Scotland. But this process is not advantageous, because there remains very much water with the tar, which can only be separated from it by being allowed to settle for some time; hence if a naked fire is to be used, it is best to do so from the first.

Sometimes the "boiled tar" resulting from the first distillation is not discharged into a tank, but is pumped out through a pipe from the steam-still into a second still, heated by an ordinary fire, so as to avoid any exposure of the hot tar to the air or evolution of disagreeable fumes.

The condensation of the escaping steam and naphtha-vapour, owing to the large quantity of the former, is rather more troublesome than when the distillation is effected with "dry" steam or with a fire. There is much more cooling needed, *i.e.*, longer worms and more cooling-water. The condensing-mixture of naphtha and water divides at once into these two constituents, which can be kept apart by overflow vessels, as will be mentioned hereafter in describing the rectification by steam of the lightest oils (Chapter XI.).

The usual yield of naphtha by this plan is 2 to 6 per cent. from ordinary tar, or 10 to 20 per cent. from cannel-coal tar. The longer the operation is continued, the more, but heavier, naphtha is obtained.

The *naphtha* obtained by steam distillation is of course richer in volatile constituents than that obtained by direct distillation of tar. But it is far from containing only such constituents as boil at and below the temperature of the blown-in steam (rarely above 150° C.); a number of much higher-

[1] *Destructive Distillation*, p. 23.

boiling substances are carried along, as shown by the following analysis:[1]—

	I.	II.	III.	
Oils up to 100° C. .	20·9	14·2	29·3	per cent.
„ 130° . .	5·9	13·2	8·0	„
„ 160° . .	8·7	19·6	15·2	„
„ 202° . .	16·0	16·6	23·9	„
Oils boiling above 202° (by difference) .	48·5	36·4	29·6	„

		Sp. gr.
I.	Naphtha from the tar of the Hamburg gas-works,	0·964
II.	„ „ „ Berlin English „	0·947
III.	„ „ „ „ Corporation „	0·932

Hence this product is not nearly so valuable as the "first-runnings" of distillation over a naked fire, and is more similar to the "light oil" of that operation.

In Scotland,[2] instead of distilling by steam, sometimes a fifth of its bulk of water is added to the tar and the whole distilled by a direct fire. Less but better naphtha than by steam distillation is said to be thus obtained. This process comes to the same thing as distilling by steam of ordinary atmospheric pressure, but does not seem worthy of recommendation, as the danger of boiling-over is very great.

Distillation by Fire.

The more usual way of distilling tar, by a direct fire, has for its primary object the removal of the non-volatile or too-little volatile constituents, which form the greater portion of tar, in the shape of pitch, and to effect a preliminary fractionation of the distillates, which are then worked up singly. It is evident that this can be done only by a direct fire, since the boiling-point of the most valuable product from tar, anthracene, coincides with that of mercury (360°).

Dehydration of the Tar.

The first condition of a quiet regular distillation is that the tar should be freed as much as possible from the ammoniacal

[1] From Kerl-Stohmann's *Chemie*, 3rd ed., vi., p. 1172.

[2] Ronald and Richardson, *Chemical Technology*, vol. i., p. 733; Mills, *loc. cit.*, p. 23.

liquor which is always mixed with it to a certain extent, and the presence of which is a disturbing element in the distillation. (The estimation of the water contained in the tar will be described at the close of this chapter.) So long as water and tar-oils boil at the same time, there is always a tendency of the liquid to "bump," or even to be jerked over explosively. This can be overcome by very cautious, slow firing; but shortening this stage of the work is certainly desirable, although it is hardly possible to do without it altogether. Hence *previous dehydration* of the tar is decidedly advisable whenever it can be done without too much trouble.

If the tar be sufficiently fluid, mere prolonged rest will separate a large portion of the ammoniacal water from it; for as the water is only mechanically suspended in the tar and is of less specific gravity, it will rise to the surface, whence it can be drawn or ladled off. Preferably very tough tar is mixed with thinner tar to facilitate the separation of the water. In many places nothing else is done for this purpose but storing the tar in several large cisterns, holding, if possible, several hundreds of tons each, which are best placed at such an elevation that the tar can be run from them straight into the stills. Whilst one of these cisterns is being filled by pumping in fresh tar, the others are allowed to rest; and from that which has stood longest the now somewhat dehydrated tar is drawn off.[1] At some of the best works a closed steam-coil is laid in the cisterns, by means of which the tar can be heated at will, in order to make it more fluid and to separate the water better. In summer there is no occasion for this; but in the colder seasons the tar is heated to 20° or 21°, sometimes up to 40°. Hardly any perceptible loss of benzol occurs at this temperature, as there is a layer of water on the top of the tar.

A more complete separation of tar and ammonia is aimed at by the invention of J. and R. Dempster (B. P. 3245, 1882). To the opening, out of which the liquor or tar passes, a suitably-shaped box is fixed, having a vertical pipe screwed therein, with an overflow cup on the top, which can be

[1] According to Watson Smith, at small works tar and gas-liquor are allowed to settle in the same tank; the tar is drawn off by a tap in the bottom, the ammoniacal liquor by one placed higher up, into their respective stills.

raised and lowered by means of a screw to suit the height of liquor in the vessel, so that it can flow over the edge of the cup down the screwed pipe into the box, and out at the outlet.

In Germany a number of gas-works employ Kunath's separator, as supplied by the Berlin-Anhalt Engineering Company (Ger. P. 15255) (Figs. 79, 80, 81). The principle of this apparatus is to spread the tar on broad overflow-spouts. The tar, slightly heated by means of the steam-pipes B B, on running over the spouts A A, separates from the water. This separation is further promoted in the vessels I., II., III., IV. by the water overflowing near the top by the lateral pipes, whilst the tar passes on at the bottom in the direction indicated

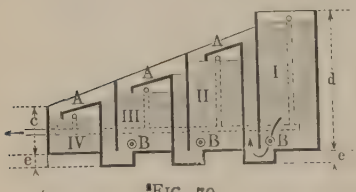


FIG. 79.

FIG. 80.

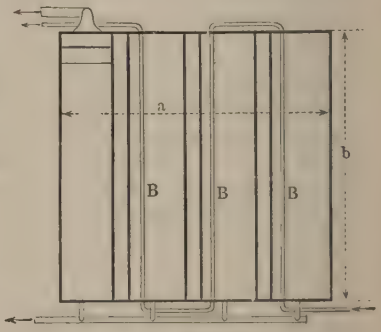


FIG. 81.

in No. 1 by the arrow, and is carried on to the top of the next-following vessel. The outlet of the water in vessel I. is situated so much higher than the spout A in the vessel II., that the difference in height corresponds to the difference in specific gravity between tar and water. There are 7 sizes of this apparatus, for separating from 1000 up to 8000 litres (225 to 1777 gallons) per 12 hours.

Similar apparatus have been described by Ruppert (Ger. P. No. 40204), also by Krayenbühl, and by Peterson and Burmeister (B. P. No. 15067, of 1887).

At smaller works Schlosser's *tar-separator* (*J. Gasbeleucht.*, 1902, p. 923) may do good service. The tar is put into a tank, placed on a cylinder with horizontally corrugated sides, and is allowed to flow over. In running over the corrugations, the

separation of the water and tar takes place more easily, and both are collected in a table below.

A similar principle appears in the process of the *Deutsche Kontinental Gas-Gesellschaft Dessan* (Ger. P. 191432). The tar is conducted downwards in an open spout, inclined at an angle of 45° against the horizon, to a point underneath the level of the liquid in a collecting-tank, in such manner that the tar, while flowing down in the spout, remains below the water flowing on its surface, and just the same also below the surface of the ammonia water already contained in the collecting-tank, until it reaches the level of the tar already separated in the latter.

As a matter of course, the separation of water and tar goes on all the more rapidly and completely, the *thinner* and less viscous the tar is, and this most thoroughly effected by moderately *heating it*. This can be done to a certain extent even in an open tank or vessel, as mentioned above, but it is done more thoroughly at a higher temperature and in such manner that the escaping vapours are condensed to a mixture (easily separating) of light oils and ammonia water. For this purpose the following apparatus have been constructed.

According to Girard and Delaire,[1] the dehydration of tar is effected by heating to from 80° to 90° in large boilers, by means of a steam-coil or jacket, or by a direct fire. The volatilizing oils are condensed. After from 20 to 30 hours the separation of tar and water is sufficiently complete, so that the water collecting at the bottom (?) of the boiler can be drawn off by a cock. The tar is now charged hot into the stills. If this description were correct, it would be precisely similar to the process described on p. 312; only it is called a dehydration instead of a distillation, as we have (assuredly more correctly) called it. But we have already stated that a division of the distilling-process into two phases, by steam and by direct fire, whether it be theoretically correct or not, does not seem to have stood the test of practical experience, for none of the largest works proceed in this manner. Girard and Delaire's description is evidently at fault in that it makes the water collect *below* the tar, which is impossible in the case of coal-tar. The same error is committed by Bolley,[2] undoubtedly from a confusion between

[1] *Dérivés de la Houille*, p. 7.

[2] *Chemische Technologie der Gespinnstfasern*, p. 27.

coal-tar and browncoal-tar, etc. In consequence of a similar inconceivable confusion, C. Vincent[1] states the specific gravity of *coal-tar* as 0·85 or 0·94!

Perhaps the most rational method of dehydrating the tar is the following, practised at one of the largest and best German tar-distilleries as the commencement of the distillation-process itself. The tar is pumped as it is into the (very large) stills until it begins to run out of a small overflow-cock placed just below the upper dome of the still, when the pumping ceases and the firing is started. Before the tar arrives at the boiling-point, it has, of course, turned quite thin, and most of the water has collected on its surface. But as by the heating the bulk of the liquid is increased and its level rises above that of the overflow-cock, the watery portion can be drawn off by opening that cock from time to time. Even if a little tar should escape with the water, no harm is done. Whatever vapours are given off during this heating must pass on to the condensing-apparatus, and are thus utilized.

According to a communication, received from Dr G. Kraemer in 1907, the method now usually practised in Germany is this. A still is half-filled with tar and this is heated to boiling. The vapours pass through a short column fed with fresh tar, which is thus dehydrated and arrives in the still freed from water. From the still it flows continuously by means of an overflow siphon into a reservoir from which the ordinary stills are fed.

A special dehydrating still, "alambic à circulation," has been patented by Th. Foucault (supplied by L. Poillon, 158 Boulevard Montparnasse, Paris). Figs. 82 and 83 show its construction. It is a rectangular box (A), heated only at one side, and divided into two unequal parts by a perpendicular partition (C), also by a slanting plate (B). The cover is formed by an inverted pyramid (K), in which circulates cold water, introduced through I, and running out at T; a gutter (F) receives the liquid condensing from the vapour upon the lower side of K. The tar is introduced through J, and at first takes its level in both compartments, as regulated by the tap E. As it is heated in the smaller compartment alone, it swells up there, rises, and at last gets up to the slanting plate B, on which it spreads out, is

[1] Payen's *Précis de Chemie industrielle*, 1878, ii., p. 944.

cooled down, and runs back into the larger compartment, whence it flows back into the smaller compartment, where it

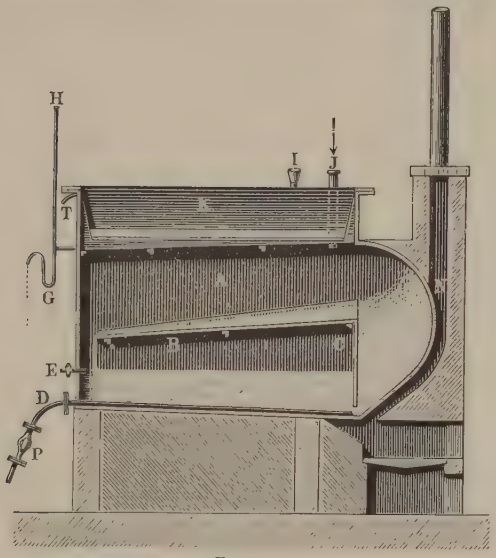


FIG. 82.

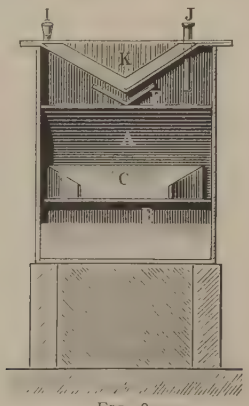


FIG. 83.

again swells up and overflows on to B, so long as any water is present. The vapours of steam and light oil which are formed

condense, on touching the cooled cover, into a liquid, which falls into the gutter F, and is carried out of the still by the siphon-tube G; the gases escape through H. After some time the circulation becomes slower; the tar ceases to froth and swell and becomes hotter. It is now perfectly quiet, and can be run off through D and P into the ordinary stills, where it is now distilled without any bumping or dangers.

The Rütgerswerke A. G. (Ger. P. 161524) dehydrate coal-tar by heating from the top downwards, first the steam-space, then the upper portion of the liquid, formed of the water floating on the top, then the lower portion, holding water in emulsion, and lastly removing the chemically combined water. Two (or three) stills are working in a set. The waste fire-gases from the lower stills are conducted first round the steam-space of the top still, which serves as a dehydrater, and then circulate round the lower part of the same. The water is thus completely separated in the upper still, and the dehydrated tar which runs into the lower stills is distilled in these much more quickly than otherwise, without fear of boiling over.

Scholvien (Ger. P. 161236, patented in the United Kingdom by Oppenheimer & Kent, B. P. 12696, 1903) dehydrates the tar by quicklime or anhydrous calcium sulphate (burnt plaster of Paris). This process is more especially intended for water-gas tar; in the case of ordinary coal-tar it will hardly come into use, for it would lead to a loss of phenols by the formation of calcium compounds. According to their German patent 163623, the tar dehydrated in this manner is distilled down to pitch. The distillate is treated with acid and alkali in the usual way and distilled again, thus obtaining in the first instance a perfectly limpid distillate, smelling faintly ethereal. When the distillate begins to show a yellow colour and oily appearance, it is caught separately, again treated with acid and alkali and redistilled. Thus a clear liquid is obtained, of specific gravity 0·860 to 0·920, boiling between 100 and 270° C. and consisting of hitherto unknown hydrocarbons. Its inflaming point is 30° C. above that of petroleum; it is specially adapted for motor engines, where it gives out 20 to 30 per cent. more power than ordinary distillates, and it can also be used as a substitute for oil of turpentine.

Dehydration by centrifugals is possible down to 1 per cent.

water, according to Menzel,[1] who speaks very favourably of this process as carried out at the Charlottenburg gas-works. The centrifugal requires 3 to 4 h.p., and the dehydrated tar can be used without any further treatment in the manufacture of roofing-felt.

Klönne (Ger. P. 196240) dehydrates the tar by grinding it by means of heatable rollers. This liberates the particles of gas-liquor enclosed in the viscid tar, and produces tar, free from gas-liquor, more cheaply and conveniently than is possible by long storage, or heating, or centrifugaling. The same inventor (Ger. P. 192535) utilizes the vapours given out by the tar when being heated for the purpose of dehydration, by employing closed store-tanks provided with arrangements for heating and for condensing the vapours evolved.

Wilton (B. P. 26910, of 1907) first heats the tar under such pressure as will prevent boiling and frothing of the contained water, and then reduces the pressure so as to liberate the water in the form of steam, at such a temperature that the main volatile constituents of the tar are not liberated and the tar, now free from water, can be distilled with ease. A small quantity of naphtha and ammonia passes over with the steam, when the pressure is reduced, as explained, but these can be easily recovered by condensing the steam.

Previous Purification from Free Carbon.

The free carbon, always contained in coal-tar to a certain extent, is troublesome, especially through forming a deposit at the bottom of the still.

E. Jacobsen[2] proposes purifying the tar previous to its distillation. If coal-tar be mixed with half its volume of carbon bisulphide, all the free carbon will separate as a powder; and if the liquid be decanted, the carbon bisulphide blown off by steam, and the residue mixed with petroleum-spirit, all the brown asphalt will be left behind, whilst the remaining liquid, the petroleum-spirit having been steamed off, will consist of an orange-coloured clear oil containing naphthalene, anthracene, etc. Similarly, coal-tar pitch can be purified from its carbon-

[1] *J. Gasbeleucht.*, 1902, 467.
[2] *Chem. tech. Repertorium*, 1869, ii., p. 107.

aceous and asphalty portions; the hydrocarbons remaining over are more easily fractionated, and a smaller proportion is gasified on heating, so that anthracene can be recovered from them with more facility. Carbon bisulphide and petroleum-spirit are easily recovered without any essential loss (?). When petroleum-spirit is added directly to coal-tar, the asphalt, which is precipitated, forms, with the free carbon and a portion of the dead oil, a tough, difficultly manageable mass; and by adding a mixture of carbon bisulphide and petroleum-spirit, part of the brown asphalt is dissolved. Hence the process should be conducted exactly as above described. [I am not aware that this process has ever been carried out on a large scale: it seems too expensive and too dangerous as regards fire, and probably a good deal of anthracene will be left in the "free carbon" and the "brown asphalt"; neither would it be easy to re-obtain the dissolving-medium free of cost.]

Lennard (B. P. 2183, 1899) also proposes removing the free carbon before distilling the tar.

Gaster (B. P. 6739, 1901), for the purpose of removing the free carbon, first distils the tar as usual until a temperature of about 260° C. is reached. The distillation is then interrupted, and to the partially cooled pitch in the still, naphtha is added, from 1 to 3 parts to 1 of pitch, in a mixing vessel provided with an outlet, of the vapours formed to a condenser. The mixture is now either at once transferred to a heated retort, or after separation of part of the free carbon by settling or by a centrifugal. In the retort the volatile solvent and the heavy oil (pitch) are separated in the shape of vapours [?] from the free carbon, and are conducted to a cooling or pitch-collecting pot, where the heavy oils (pitch) are collected, and, if necessary, are mixed with other oils for obtaining the desired quality of the pitch. [I am not responsible for the apparent inconsistencies of this description, which in the patent specification goes on a good deal longer, without throwing more light on the above.]

Witt[1] reports on carbon-free coal-tar, exhibited in Paris, 1900, by Johan Ohlsson's Tekniska Fabrik, of Stockholm, a clear, transparent, brown fluid, the use of which he was not able to ascertain. The carbon, exhibited at the same time, had not the appearance of soot, but of graphite, and might probably

[1] *Chem. Ind.*, 1901, p. 326.

serve much better than the "graphite" from gas-retorts for electric arc carbons, crucibles, etc. [According to G. Kraemer, the iron present in such carbon obtained from tar by means of solvents is an obstacle to its use.]

Purification of Blast-furnace Tar from Solid Impurities.

Specially for the manufacture of pitch from *blast-furnace tar*, Craig (B. P. 2942, 1907) prescribes to dehydrate the tar by heating, and then to treat it in a centrifugal separater, or to pass it through a filter-press, whereby from $7\frac{1}{2}$ to 10 per cent. of "clayey" sludge, containing 50 to 66 per cent. of ash, is removed. The purified tar is subsequently distilled in the usual manner.

Construction of Tar-stills.

Only one material is suitable for tar-stills, viz., wrought-iron. Cast-iron stills would be less subject to burn away and to mechanical injury in clearing them of coke; but they cannot be easily made of considerable size. Both the difficulties and the cost of casting increase very rapidly with an increase in the size of hollow objects; neither can a perfect uniformity of structure be expected in the case of unusually large castings. Even when they are made as upright loam-castings and with a large feeding-head, an air-bubble may very easily remain, and, in the case of vessels exposed to a direct fire, cause in that place a most dangerous tendency to crack. But even a faultless casting is still very liable to crack, and must never be set without a curtain-arch over the fireplace: nevertheless any carelessness of the fireman will cause it to crack; and the mischief will then be great in proportion to the size of the vessel. Wrought-iron vessels, on the other hand, cannot be cracked by incautious firing, at least not in consequence of sudden changes of temperature, although an explosion from an excess of pressure, if all outlets are stopped up, is still possible. It is true that the plates are more easily burnt by the first action of the fire than cast-iron; but this must, under any circumstances, be provided against by a curtain-arch. It takes very gross and long-continued carelessness on the part of a fireman to burn the plates of a properly set still, whilst even

the best workman cannot always help the cracking of a cast-iron still.

It should be further noticed that the metal of cast-iron stills must be at least four times as thick as the usual boiler-plates; this makes the former much more expensive than the latter and increases the consumption of fuel. Lastly, wrought-iron stills can be repaired by patching, or by putting in fresh plates, whilst similar repairs are nearly always excluded in the case of cast-iron.

Cast-iron is, however, the proper material for the still-head, the cooler, and other parts not exposed to the risk of cracking; it resists the action of the ammoniacal vapours better than wrought-iron. The connexion between the still-head and the cooler is best made of wrought-iron, as this is tougher, and the risk of cracking through the changes of temperature is very great just in that part.

If wrought-iron stills are protected, by means of a "curtain-arch," from injury by the first heat of the fire, they last very long, provided they are properly treated, especially in cleaning out. A new still should go at least four years without any great repairs, and as long again after each thorough repair. The plates burn through most easily at the bottom, where the flame issues from underneath the curtain-arch, if the latter does not reach right through. Where this is the case, so that the still-bottom is not touched at all by the flame, and is only as it were in a hot-air bath, the stills may last much longer than the above-mentioned time.

Stills worked only for soft pitch last much longer than those worked for hard pitch.

As curtain-arches, etc., cause more fuel to be consumed, some prefer doing without them, and strive to prevent damage to the still-bottom by frequent cleaning out. According to G. Kraemer (priv. comm.), long practice has proved to him that curtain-arches may be dispensed with if the stills are placed sufficiently high (3 to 6 feet) above the fire-grate.

The following general rules should be observed in constructing the stills:—The *thickness of the plate* of the sides as a rule need not be over $\frac{3}{8}$ in.; the very greatest thickness, for 40 or 50 tons of tar, should be $\frac{1}{2}$ in. The upper plates should be quite as thick as the lower plates, since they wear out rather more quickly

(see below). The top and bottom are made rather thicker than the sides, especially where a vacuum is to be employed; in this case the top plates should be at least $\frac{1}{2}$ in., the bottom plates $\frac{3}{4}$ in. thick.

Of course the plates must be very well riveted and caulked; but in spite of that the seams of new stills often show a tendency to leak at the end of the distillation, when the temperature has risen very high. This is seen by a flame running along the seams or rivets; it always occurs at the bottom, and can be cured by fresh caulkings. Even without that, coke soon sets into the seams and makes them tight; hence such leaking is mostly noticed after a thorough cleaning of the stills. In any case it does not endanger the safety of the still. The same thing holds good of the stills for light oil and other similar ones, to be mentioned hereafter.

Much difference of opinion exists as to the best *shape of a tar-still.* Formerly anything was made to answer, especially old steam-boilers of various shapes. Mostly this was bad economy; increased consumption of fuel, longer time of working off, frequent repairs, and frothing over of the contents of the still amounted to several times the cost of a new tar-still of the best pattern. But there is much dissension upon the question, What is the best pattern for a tar-still? The following is a description of the various forms of stills found by me on my visits at well-conducted works in different countries.

The form of still almost universally met with in England, and also at the majority of German works, is an *upright cylinder*, of nearly equal height and diameter, with a dome-shaped top and a concave bottom, *i.e.*, equally curved upwards in a dome-shape. This concave bottom is preferable to a flat bottom, on account of its greater stiffness and larger heating-surface, and because the iron can better expand and contract with the inevitable great changes of temperature to which it is exposed. Convex bottoms would have equal advantages, but would not present such a favourable proportion between the heating-surface and the contents of a boiler as concave bottoms; they are not so easily set, and the pitch could not very well be run out completely by means of a cock in a lateral direction.

Such stills are always made of considerable size, both to save labour for attendance and because the separation of the products

according to their boiling-points is easier the larger the quantity treated in each operation. Rarely are smaller stills used than those for a 6-ton charge; but they are sometimes preferred because a charge can be worked off in 10 or 12 hours, and night-work thus becomes unnecessary. But the large works usually have larger stills:—in England, holding from 10 to 20 tons, rarely more; in Germany, 20, 25, or even 50 tons. It is doubtful whether such very large stills are the best; 20 tons seems the most convenient size; and more recently 15-ton stills have also been frequently erected in Germany.

Watson Smith advises trying the tightness of each still by putting it on its seat, connecting it with a steam-boiler, closing all openings, and blowing in steam at 2½ atmospheres' pressure; it should not leak anywhere then. (Evidently an air-cock must be left open till all the air has been expelled.) He also observes that there is usually some difficulty in fixing the cast-iron still-head, inasmuch as the cover is mostly made of several pieces overlapping each other at the seams, and thus presenting obstacles to a tight joint with the flange of the still-head. This can be avoided, either by making the top piece out of one plate with a circular opening for the head; or else, if the top is constructed of several pieces, by making a wrought-iron ring to fit the central opening (previously provided with rivet-holes), hammering it down while red-hot, so hot that it adapts itself to all the uneven places of the joints, marking the places for the rivets, taking the ring off, punching the rivet-holes, putting the ring on again, and riveting it fast to the top. The inner border of this ring, projecting into the central opening and left quite smooth, serves for bolting on the still-head.

The German tar-distillers do not agree with all these assertions. In their opinion a high-pressure test is useless, as the stills are never subjected to such pressures, and the test itself might damage the stills; it is sufficient if the stills hold tight at 7 or 14 lb. pressure over that of the atmosphere. But the quality of the plate for making the bottom is all-important. If possible its breaking-strain should be tested before using the plates. The construction of the bottom, as shown in Fig. 84, is that of a semi-globe of the same diameter as that of the cylindrical part; the edges are turned up and are riveted to the cylinder-shell. This turning-up makes the bottom more elastic,

without sacrificing its strength, and it avoids the cuneiform space between the bottom and the cylindrical portion, which soon chokes up with coke, thus causing the iron to get red-hot and to burn through. In the case above shown the running-off tap can be fixed in such manner that all the pitch comes out.

Both bottom and top of the still are made in Germany of a central cap and four or five segments, joined by a double row

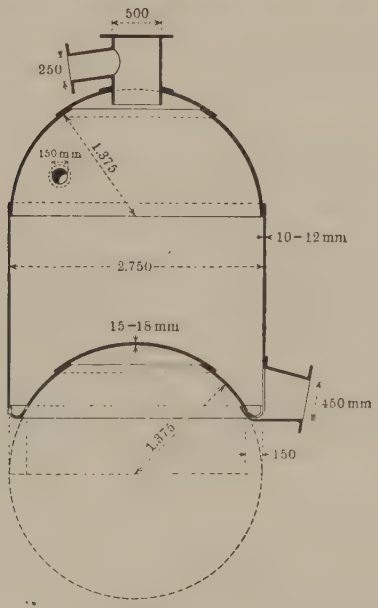


FIG. 84.

of rivets; thus the difficulties mentioned by Watson Smith as to fixing the still-head are entirely avoided. Sometimes the bottoms even for stills of more than 8 ft. diameter are made of one piece; but these are less stiff than those made of several pieces.

Formerly the joints were made with the well-known rust-cement, or modifications of it. But asbestos board is far better than this, both for the flanges and the manhole lids, etc.

Some works employ a very different shape of still, viz., *horizontal cylinders* similar to steam-boilers. They are of

course less in diameter (rarely above 7 feet), but longer, than upright stills. It would seem that they require more fuel than the latter form of stills, and that the tar has much more tendency to froth over in them during the first period of the distillation.

At a German works I found such horizontal stills, holding 18 tons and provided with two or three still-heads, which were pronounced to work very satisfactorily. At another factory I saw horizontal stills, holding 22 tons, which required 48 hours for distilling off a charge, apart from the time for filling and cooling down, so that only two charges could be made per week. The plates have a thickness of 12 mm. at the bottom, and 14 mm. at the top (that is, slightly below and slightly above $\frac{1}{2}$ in.). They are made thicker at the top, because they suffer more where they are not in contact with tar or pitch, and are more reduced in thickness by working than the bottom plates—an observation which I have found confirmed in the case of English upright stills. The setting of the horizontal stills is best made in such a way that the flame does not directly touch the bottom of the still for about two-thirds of its length, but is kept off by an arch perforated with pigeon-holes; the last third of the bottom is heated by the direct flame, the bottom of the flue being 12 inches below the lowest part of the still.

In America the most usual shape of tar-stills is also that of horizontal cylinders, made of $\frac{5}{16}$ in. steel plates, of about 2000 gallons capacity, with only one row of rivets along the top.

In my opinion, horizontal stills are altogether inferior to upright ones; they work much more slowly, and they consume incomparably more fuel than the latter. At a works where horizontal stills are used, the manager told me that 1 ton of coal, or an equivalent of other fuel, would distil 5 tons of tar; whilst at several other works, where upright stills are used, I found that only *one-third* of that amount of fuel was consumed.

Stills of a very peculiar shape are employed at the Paris gas-works. They are *waggon-shaped*, with an incurved bottom, and edges very much rounded (Fig. 85), holding only 1440 gallons of tar. The flues run twice round the sides of the stills.

This shape, I am informed, is preferred because it causes the least injury to the metal in contracting and expanding with the changes of temperature. But such injury has not been observed where the usual upright cylindrical stills are at work; and the Paris shape has from the first the disadvantage of requiring two running-off cocks, one for each side (at *a a*). These stills are set so that the bottom is not touched at all by the fire, which circulates twice round the sides. In the lower flue the flame does not impinge directly upon the metal, which is protected by thin firebricks; in the upper flues these are wanting. Everywhere else I have found the flame

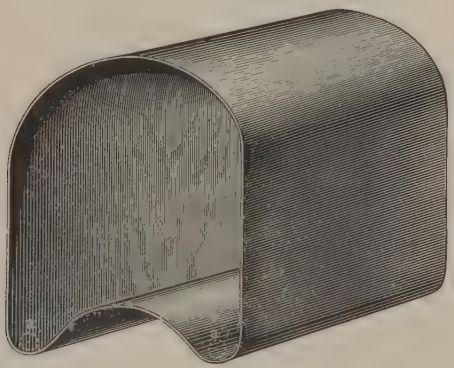


FIG. 85.

(which has expended its greatest heat upon the curtain-arch beneath the still-bottom) heating the sides of the still without any firebrick lining and without doing any injury to the still. The stills at those works do not show the arrangements mentioned by Girard and Delaire[1] and by Wurtz,[2] by which, as soon as the level of the tar sinks too low, the upper flue is shut off and the flame is only allowed to circulate in the lower flue. But anyhow the flues heat only the lower part of the still; so that such a complicated arrangement is not called for. Even the upper flue is built in such a way that the level of the pitch at the end of the distillation is still above it—which is not very difficult to manage, since the bulk of the pitch is at least

[1] *Dérivés de la Houille*, p. 8. [2] *Matières colorantes*, p. 23.

half of that of the tar. Kissel (*Z. angew. Chem.*, 1893, p. 61) prefers this shape to all others.

Another shape of waggon-still is shown in Figs. 86 and 87,

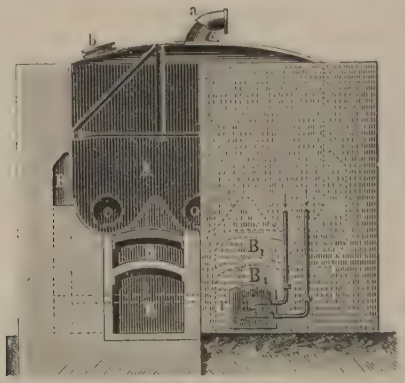


Fig. 86.

according to Engler (*Dingl. polyt. J.*, 1886, vol. cclx., p. 435), as employed in the Baku petroleum-refineries. They are up to 23 ft. long, 13 ft. wide, and 10 ft. high. *a a* are the still-

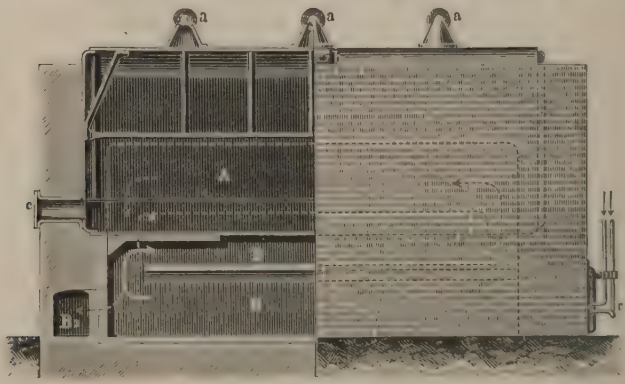


Fig. 87.

heads; *b* a manhole; *c c* three outlets for the residues. The arrangement of the internal stays is clear from the diagrams. There are two fireplaces (*r*) supplied with "astatki" (pp. 258 *et seq.*; I have seen tar-stills worked with creosote oil, when this was

unsaleable!); the flame first passes through the arched-over flues B, B_1, returns at the still-end to the fore part, rises up, travels again backward along the sides of the still, then downward and through the flue B_2 into the chimney.

J. Maxwell (B. P. 3640, 1882) places vertical pipes within the stills, with or without the use of a compressed-air tube, for the purpose of facilitating the separation of water, oil, and other liquids from the tar while undergoing distillation.

Stills with mechanical agitators will be described in a later part of this chapter.

The various parts belonging to a tar-still are best described along with an explanation of Figures 88 to 90. These represent a 25-*ton still*, the details of which, as well as those of the setting, are not copied from a particular plant existing at a factory, but combine those features of all the apparatus observed by myself in England and Germany which seem to me most practical. But each single part, described or drawn here or hereafter, is actually in use at one or another of the largest and best works.

Fig. 88 is a cross-section along the line E F of the plans; Fig. 89, a plan laid through C D of Fig. 88; Fig. 90, a plan of the still itself, along the line A B of Fig. 88,—all $\frac{1}{50}$ of the natural size. The still is 9 ft. 10 ins. wide, and 11 ft. 6 in. high (without the dome), made of $\frac{3}{8}$-inch or $\frac{1}{2}$-inch boiler-plate. The inward curve of the bottom is about the same as the outward curve of the top: both of them are sometimes made much higher than shown here. The still may be set with a slight slope towards the outlet-cock *a*, which in any case is placed as nearly as possible just above the bottom, or even in the flat part of it. This is absolutely necessary if hard pitch is made; where only soft pitch is made, as is usual in Germany, it is not so essential.

The still is heated by a fire-grate (*b*) adapted to the special quality of the fuel. The usual fuel is small coal (slack); sometimes, especially at gas-works distilling their own tar, coke is employed, by which, however, the still-bottom may be injured unless completely protected by a curtain-arch, or unless steam be introduced at the end of the operation. Sometimes, if the heavy oil is not easily saleable, it is employed for firing the tar-stills; many arrangements for this purpose have been described in Chapter IV.

The fireplace is accessible from without by a door (*c*). Where

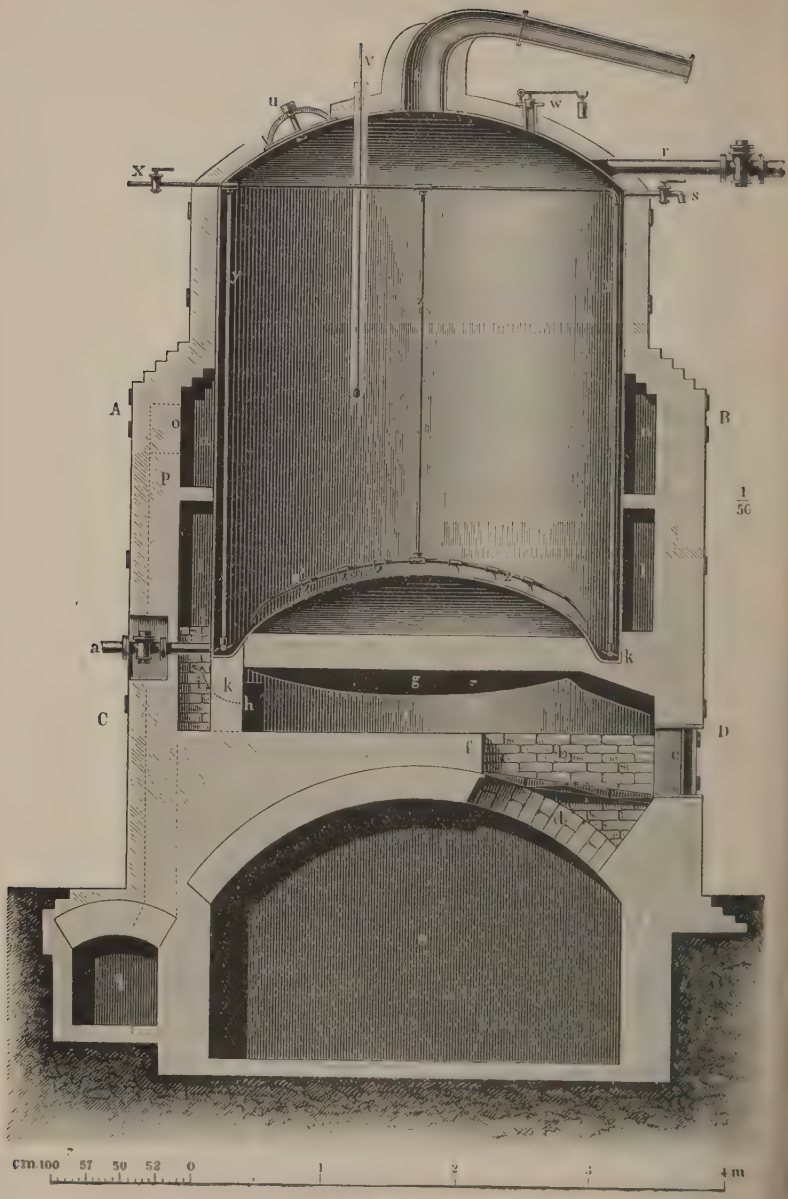


FIG. 88.

there are a number of stills, all the doors are arranged in the same lines, opposite to the sides where the pitch-cocks *a* are placed. Usually the ash-pits under each grate communicate with the outer air by an opening below the fire-door. But in our diagrams is shown the arrangement at one of the largest English works. Here the ash-pits are closed below the fire-doors, and all of them communicate by an opening (*d*) with a large overarched passage (*e*) running along the whole set of stills

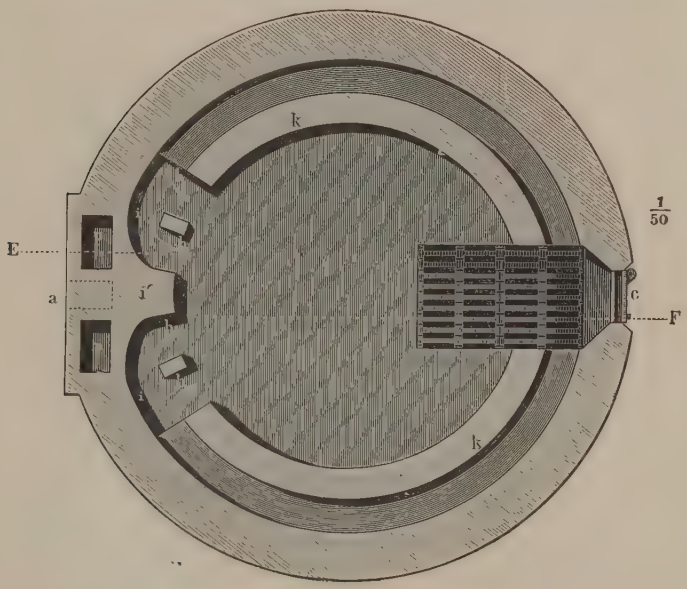


FIG. 89.

and only accessible from the two extremities; this affords perfect security against fire in case of the tar boiling over and running out of the receivers. It is true that other precautions can be taken against this danger, such as constructing the receivers in the manner to be described below, where the tar, even if it boils over, cannot get at the still-fires; but the arrangement shown here will also act in the case of accidents to the pipes and, especially, to the still-head, for with it the vapours issuing in great force cannot take fire at the ash-pits. Moreover,

the underground passage *e* permits great cleanliness. It is useful to place a steam-pipe below each fire-grate, to increase the draught, to prevent overheating of the grate-bars and the fire-bars, and thus to avoid the formation of fluxed cinders.

The flame travels over the fire-bridge *f*, and under the arch *g*. This arch is sprung barrel-shaped from the annular wall *k k* on which the still is seated, and completely shuts off the still-bottom from the flame. Thus the space between *g* and the

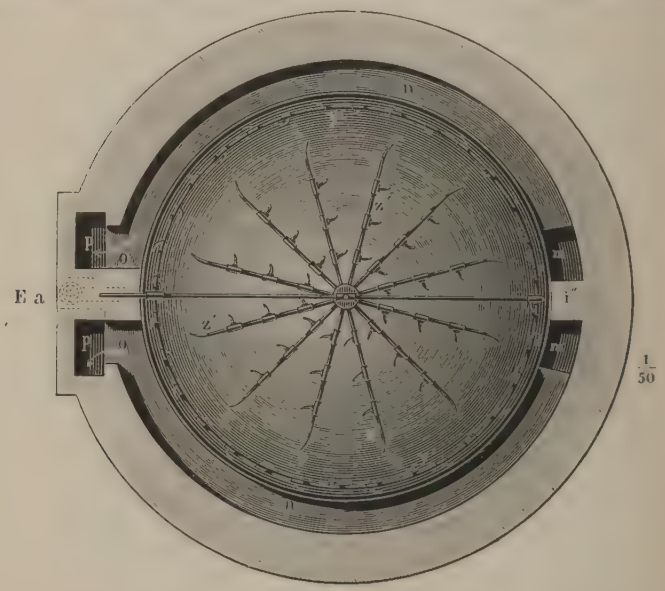


FIG. 90.

still-bottom is an air-bath, kept very hot by the flame below *g*, but never excessively so. So much heat is imparted to the arch *g* that at the end of the operation no firing is needed, especially if steam or exhaustion be applied. The weight of the still resting upon the annular wall *k k* enables this all the better to support the pressure of the curtain-arch *g*, which is otherwise independent of the brickwork of the fireplace, and can be easily renewed when it is too much burnt out. The flame now travels on through four holes (*h h*) into two vertical flues (*i i*), and arrives at the cylindrical shell of the still. The

solid pillar *i''*, between the flues *i i*, is continued to the top. Through this pillar passes the pipe connecting the pitch-cock *a* with the still, protected from the fire, but kept warm by the flues *i i* and *p p*. This pipe should be at least 12 ins. wide, to prevent choking-up. The pillar *i''* forces the flame to divide into two currents, which pass round the lower part of the still in the annular flue *l l*, are prevented from uniting in front by the pillar *i''*, pass through the flues *m m* into the upper annular flues *n n*, return to the back part, and enter through *o o* into the downcast-shafts *p p*, communicating with the main flue *q*. The shafts *p p* are provided in suitable places with dampers, by which equal heating of both sides of the still can be secured. For shallower stills a single annular flue would be sufficient; its downcast-shafts would have to be arranged in front, at each side of the fireplace. The best width of the annular flue is from 9 to 12 ins.

The outer wall, as far as the flues reach, should be at least 14 ins. thick, and should be strengthened by several iron bands, shown in Fig. 88. Above the flues the still is surrounded by a 9-in. brick jacket to prevent cooling; the brickwork continues along the whole top, and preferably also up to the top of the still-head *t*. Such a protection against cooling is all the more needed if the tar-stills are exposed to the air, or merely covered by a light corrugated iron roof, etc. This, the most usual, style causes any explosions or fires to be less destructive than if the stills were placed in a substantial building. It is advisable in that case to protect the brickwork of the stills against rain by a coat of molten pitch.

The mountings of the still are as follows:—A cast-iron *supply-pipe* (*r*, Fig. 88), closed by a slide-valve or cock, is provided for running-in the tar. It is best rather wide, say 6 ins., so that much time may not be consumed in filling the still. Where the tar is not pumped, but run in from a high store tank, a simple hole will do, afterwards closed by a screw-plug, or even the manhole. There may be a special hole, through which the depth of the tar can be gauged; but an *overflow-cock* (*s*) of 1-in. bore is preferable. As soon as tar comes out of it the feeding is stopped and *s* is closed. We have seen on p. 318 that, during the heating up, the water collecting on the top of the tar can be removed from time to time by opening *s*, which greatly assists

the work. If the tar is pumped by compressed air, in which case the pressure-vessel serves for measuring its quantity, the gauge-hole and overflow-cock are unnecessary, as the filling-pipe serves at the same time as overflow (p. 312).

The cock *a* (Fig. 88) serves for *running off the pitch;* it will be described more exactly hereafter. Instead of connecting it, as is here shown, by a 4-in. pipe with the still, the latter is better provided with a 12-in. pipe projecting through the brickwork, and in this the cock *a* is fixed. If the setting is similar to that shown here, the pipe is always hot enough for the pitch to remain liquid. But it is possible to work altogether without a cock, by forcing up the pitch through a vertical delivery-pipe by means of steam (*cf.* below).

The vapours are carried away by the cast-iron *still-head*, *t*, which decreases in width from 12 ins.[1] down to 6 ins., and is then continued into a 6-in. metal pipe leading to the condensing-tank. Sometimes a gutter is provided inside the still-head, at its base, to conduct directly outwards any liquid condensing in the rising part of the head, so that it cannot drop back into the still, where it might cause frothing-up; but this is hardly necessary if that part of the still-head is surrounded by a bad conductor of heat. In some places they put a steam-pipe into the still-head, in order to remove obstructions by blowing through it. But a still-head of such a width cannot very well become obstructed if it has a little fall. As to the connexion of the still-head with the still-top, we have described it on pp. 326 and 327.

Every tar-still must have a *manhole*. We have represented this at *u* (Fig. 88), like a steam-boiler manhole, closed by a cover fixed on by an arm and screw-bolt; the joint is made by a ring of asbestos packing. In Fig. 84 it is shown how the manhole is combined with the still-head, which saves cutting a special opening in the still-dome. The lower side of the manhole lid is best made to slope towards a centre, where an open spout leads to the top of the condensing-worm. The object of this is: to prevent the water condensing there in a liquid form from dropping into the contents of the still and causing these to froth over. Anyhow, this water, condensing both there and on

[1] Dr Kraemer (priv. comm.) that he considers twice that width, *i.e.*, 27 ins. at the bottom, to be preferable for still-heads.

other fittings, should not be allowed to run down the sides of the still, where it might induce a corrosion; this is done by allowing these parts to continue an inch or so into the inside of the stills. In some places the manhole lid is made to serve at the same time as a *safety-valve*. It is then a plate, loosely laid upon a riveted neck, and joined to it merely by some cement which does not become too hard. If the pressure within the still should for some reason or another mount too high, the lid will be thrown off before any other damage can occur.[1] In America some tar-stills are provided with a steel pin loosely fitting into a hole in the still-cover; when there is pressure in the still, the pin is ejected, vapours issue from the hole, which is a signal for opening the fire-doors and blowing steam through the worm. Unless some such contrivance is provided, there should be a proper safety-valve present, as delineated here at *w*; but many tar-stills are found without one. A very useful precaution consists in providing a side branch to the safety-valve, which permits any tar that boils over to run to some safe place away from the still, preferably back into the tar-pit.

Hamilton (*Chem. Trade J.*, xxi., p. 87) shows a cast-iron valve, Fig. 91, where *a* and *b* are ground together; the weight (not shown here) rest on *a*. Fig. 92 represents a cast-iron valve used in Germany. A is a case with removable cover and two 6-in. branch-pipes. On the turned bottom fits the turned plate B with guide C, passing through the stuffing-box D. The valve is fixed to the still at E; at F is fixed a pipe leading to a somewhat distant reservoir. The joint between A and B is made with asbestos packing. In case of pressure within, the plate B rises up and the vapour escapes through F. Near the rod C there may be an electric contact for indicating its rising.

Hoffmann's safety-valve for tar stills, petroleum tanks, etc., sold by the Chemische Fabrik Salzkotten, is described in *Chem. Ind.*, 1905, p. 434. This valve automatically opens when a certain pressure exists within the apparatus, and below it

[1] Watson Smith (*J. Soc. Chem. Ind.*, 1882, p. 342) doubts whether this contrivance would be efficient—either it would be too tight, and thus not act at all, or else it would be too loose, and thus allow vapours to escape at the end of the process. But I am acquainted with a very large and excellently managed factory where the above-described arrangement has worked perfectly for a long time.

within the still, a thin-meshed metallic tile prevents the striking-in of a flame which may be formed by the escaping gases.

If a *thermometer* (*v*, Fig. 88) is used, it should be placed in an iron tube closed at the bottom and filled with iron filings or mercury; it should reach half-way down the still. In lieu of this, some works have pyrometers of various constructions, mostly not very reliable in their indications. Unless steam be applied in the last stage of the process, a mercurial thermometer cannot be used, since mercury boils at 360°; in that case it must first be taken out of the iron tube. It should not be forgotten that mercurial thermometers which have been exposed to a

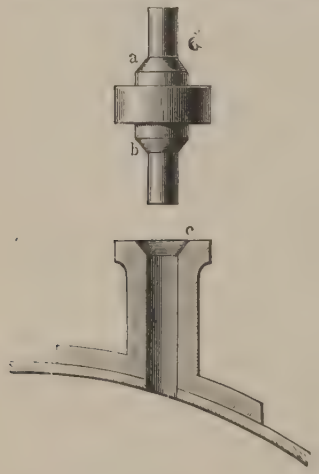


FIG. 91.

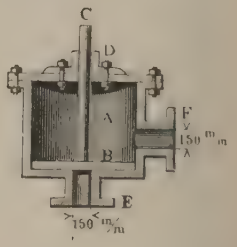


FIG. 92.

high temperature for some time vary their fixed points considerably, owing to deformations of their bulbs; such variations have been observed to extend to as much as 14°. Hence they must be compared with a standard thermometer from time to time; otherwise mistakes in the working and disputes with buyers may occur. This of course holds good of all thermometers used at tar-distilleries.

In German works the distillation is rarely carried on by the indications of the thermometer: the work is done by means of practical indications, to be mentioned below, and by the specific gravity and behaviour of the distillates.

The following precautions should be observed *in fixing pipes and mountings to the stills.* The iron is mostly corroded in those places which are not in contact with tar—that is, at and near the top; this shows that not the tar itself corrodes the iron, but the vapours, and still more condensed ammonia-water, more particularly by the ammonium sulphide. Köhler (*Z. angew. Chem.*, 1894, p. 513) found the worst corrosion where, in consequence of joints leading outwards, the plate was cooled, as at the manhole and at pipes flanged on to the still, where the thickness of the iron had diminished from $\frac{1}{2}$ in. to $\frac{1}{8}$ in. This was done away with by carrying the pipes 6 ins. into the still, and protecting them against cooling on the outside.

Care should also be taken that the thermometers, valves, manholes, etc., are inserted absolutely tightly. If this is not the case, benzene vapours will issue in the first part of the process, and as these form an explosive mixture with air (in the proportion of 1 benzene to 35 air), bad accidents might occur.

The reader will notice in our diagrams (Figs. 88 and 90) a system of *steam-pipes* (*x y z*). We shall see afterwards that the majority of works now employ steam, mostly superheated, for finishing the process. This is usually done by means of a cross-shaped tube with perforations for the issue of the steam. Here we have shown the more perfect arrangement patented by Trewby and Fenner (No. 3613, Sept. 9th, 1879). The steam is introduced by a 1-in. pipe with tap (*x*), which sends down three vertical branches (*y z y*) inside the still. The tubes *y y* communicate with an annular-shaped tube, *y'*, placed in the lowest part of the still, and *z* with a system of branch-pipes, *z' z'*, covering the whole still-bottom. Both *y'* and *z z'* are provided with a large number of open, slightly bent outlet pipes with contracted ends. Thus the steam is divided into many thin jets, ranging all over the bottom of the still, which prevent its overheating and carry away the vapours of the heavy hydrocarbons. Owing to the large surface of the steam-tubes, the steam is superheated before issuing, and a special superheater is unnecessary.

Later on, H. W. Fenner (B. P. 13629, of 1884) combined the application of stirrers with that of steam, by providing a hollow shaft, passing down the centre of the still, with branch-pipes for

distributing the steam, the whole system being made to rotate by suitable gearing.

One of the usual ways of setting tar-stills in England is shown in Fig. 93.[1] Here there is no curtain-arch at all; the fire of the grate *a* passes through the holes *b* in the annular wall *c*, and once round the still in the flue *d*. Sometimes the annular wall

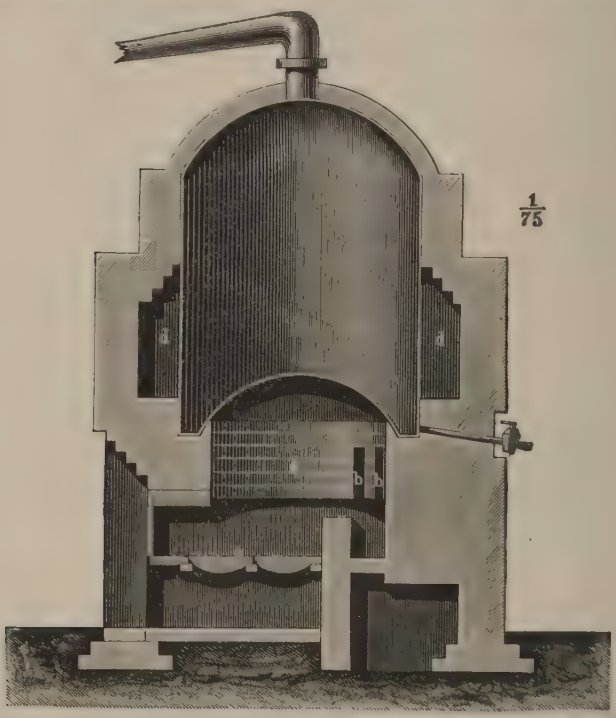


FIG. 93.

which supports the still is strengthened by iron bearers, which probably do not last very long.

At one of the largest English tar-works they have stills of

[1] From *Chemistry Applied to the Arts and Manufactures*, by Wm. Mackenzie, vol. i., p. 499. The other figures found in the same place, taken from Bolley's *Technologie der Gespinnstfasern* (pp. 210 *et seq.*), do not refer to the distillation of coal-tar, but to brown coal-tar.

the shape sketched in Fig. 94, which have been working there for a number of years and give the fullest satisfaction. It will be noticed that the rise of the bottom is very much greater than in the stills already figured, so that, in fact, the crown of the bottom dome is quite half-way up the cylindrical portion of the still. This causes the heat of the fire to penetrate well into the interior of the mass of tar or pitch, and keeps the level of the pitch at the end of the distillation at a convenient height

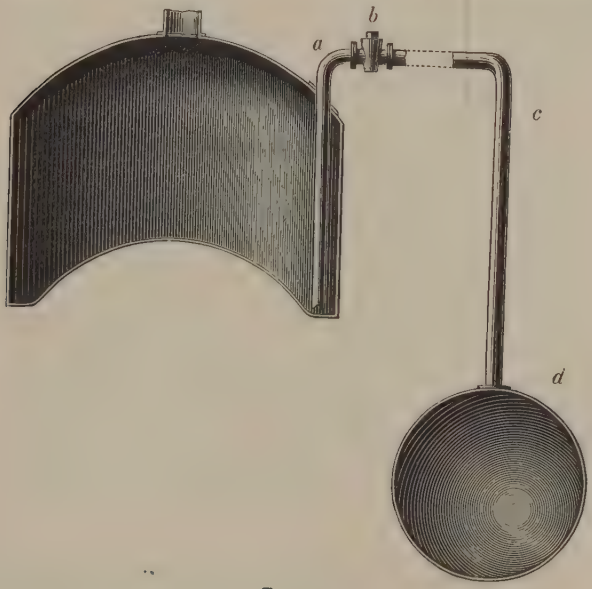


FIG. 94.

above the flue. These stills hold 14 tons of tar and require sixteen hours before running off the pitch, so that they can be charged fresh every day. In lieu of a running-off cock or valve there is a pipe (*a*) reaching down to the lowest part of the still, and continued outside in a cock (*b*) and a branch (*c*), descending into a closed tank (*d*). At the end of the distillation, and after the pitch has been softened, as may be required, by pumping tar-oils back into the still, a vacuum is produced in *d*, and after opening the cock *b* the pitch will rise through *a* and *c* and flow into *d*.

These stills require only 1 ton of coal or ½ a ton of creosote-oil, for distilling the whole charge (14 tons) of tar.

Similar stills are used at another of the very largest English tar-works; they hold 10 tons. Recently some stills have there been made to hold 20 tons, keeping to the same horizontal section and curve of top and bottom, and merely making the cylindrical portion so much higher; there seems to be a saving of fuel in the latter case. The 10-ton stills require 12 hours for distilling, 3 hours for cooling down till the pitch can be run off, and another 4 hours for filling. The firing is here (as in some other works) exclusively done by means of creosote oil, of which only 50 to 60 galls. are consumed in working off a 10-ton still, which must be considered a very good result.

From a communication kindly made to me in 1885 by Mr John Wyld, of the Bradford Corporation Works at Frizinghall, it appears that at one or more works in that neighbourhood the system of firing by gas-producers was applied to tar-stills, but it is not stated whether it was found to possess any advantage. There is no reason why it should not answer, as the firing could be more easily regulated; but I should not expect to find any saving of fuel by that method.

H. W. Fenner (B. P. 13630, of 1884) forces the flame to touch the bottom and sides of the still in a particular manner.

The plant described by Toldt (*Chem. Zeit.*, 1898, p. 258) does not show any special features.

Louis Schwarz & Co. (Ger. P. 150229) describe a new way of setting tar-stills, which is to avoid the drawbacks connected both with the solid arch below the still-bottom, as shown in Fig. 88, p. 333, and with the unprotected bottoms, as shown, *e.g.*, in Fig. 93, p. 340. The former arrangement involves a considerable loss of heating power, the latter leads to the formation of coke. The new invention starts from the fact that a coating of coke is much more easily formed on the bottom than on the perpendicular side-walls of the still. It retains the protecting arch, but between this and the still-bottom a hollow space is left, which is connected on one side with the annular flue round the sides of the still by a tube, passing through the still itself, on the other side with the exit flue by means of a down corner. The heating-gases thus first pass through the annular flue round the still, and then underneath the bottom, without

subjecting this to injurious overheating, while the tube passing through the retort still further increases the heating surface.

Condensing-Apparatus.

Girard and Delaire (*Dérivés de la Houille*, pp. 8 and 10)

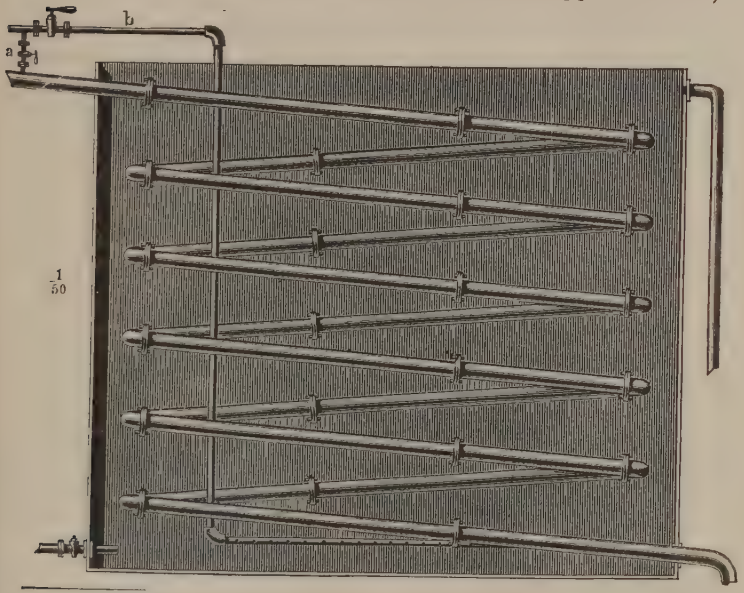


FIG. 95.

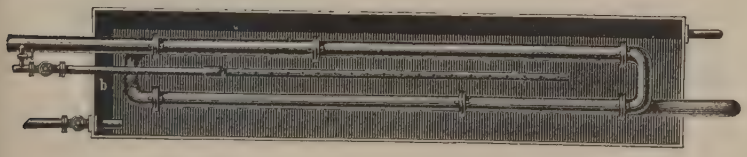


FIG. 96.

state that sometimes a still is provided with three condensing-worms, each regulated by a stopcock, and consecutively employed for the different fractions. None of the works known to me use that kind of apparatus, the object of which is not very clear, since the separation of the fractions need not commence in the worms, but can take place in the receivers.

I have never observed more than one condensing-worm; but very different kinds are used. The English works mostly employ cast-iron pipes, in lengths of 9 and 6 ft., from 4 to 6 ins. wide, and connected by elbow-pieces (Figs. 95 and 96). The whole is contained in a wrought-iron tank and is supported by strong iron stays (not shown in the diagrams). The tank being rather narrow, two worms, belonging to different stills, are occasionally placed in it. Formerly the elbows were sometimes provided with cleaning-out holes; but these are quite unnecessary, if the pipes have sufficient fall and if the tank at the end of the process is kept warm. But it is always advisable

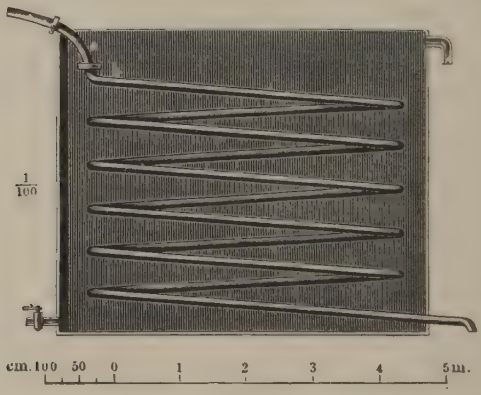


FIG. 97.

to put a steam-pipe (*a*) in the top pipe, so that the worm can be purified by blowing steam through it in case of need. Anyhow there should be a steam-pipe (*b*) for heating the water surrounding the worm.

At some English works the horizontal section of the cooling-system is not, as here shown, oblong, but square; this entails the use of very large water-cisterns to contain the worm.

The German works prefer worms made of wrought-iron or even of lead. In the latter case the cast-iron pipe *a* coming from the still (Fig. 97) must be continued at least a foot below the level of the cooling-water, and the lead pipe *b* commence there; otherwise the latter might easily be melted at the end of the process by the heat of the vapours in the part not cooled by

the water. We cannot see any reason for recommending lead worms for tar-stills.

The majority of German works prefer drawn wrought-iron tubes of 2 ins. bore, bent in the shape of three-quarters of a circle (Fig. 98) and connected by screwed-on flanges. With

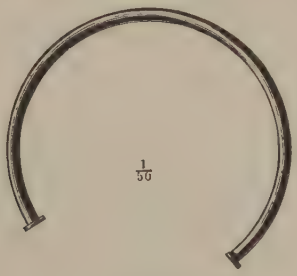


FIG. 98.

these there are no uneven places at the joints and no sharp angles as with the cast-iron worms. Even better than these tubes are wrought-iron worms each made in a single piece, as supplied by some Rhenish ironworks. These worms are always contained in circular iron tanks provided with a steam-pipe. Wrought-iron or lead worms cool better than those made of cast-iron, owing to the less thickness of metal. Their narrowness is a

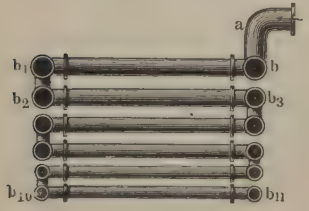


FIG. 99.

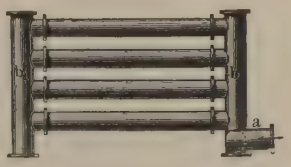


FIG. 100.

drawback, which is, however, of not much consequence where the distillation is carried on by the help of a vacuum. The thorough cooling taking place in such narrow wrought-iron tubes is all the better for keeping up the vacuum.

Engler (*Dingl. polyt. J.*, ccix.) describes the following system of cast-iron refrigerators, frequently used at the Baku petroleum-refineries (Figs. 99 and 100). There are always four pipes in a

horizontal plane, joined by a cross-piece (b, b_1, b_2), etc., and six such systems one above another, altogether 24 pipes, with a total length of 200 to 300 ft.; the top pipes have a width of 8 ins., the middle ones 7 ins., and the bottom pipes 5½ ins. The vapours enter through a, spread on the cross-piece b, pass across through four pipes to the second cross-piece b_1, then downward to b_2, back again through four pipes to b_3, and so on down to the outlet at b_{11}.

The total length of condensing-pipes is calculated in England at from 140 to 200 ft. per still. In Germany the refrigerators are about 7 ft. wide and from 7 to 10 ft. deep, with narrowly coiled worms, making the length of pipe from 200 to 300 ft., according to the size of the stills.

As *cement* for the joints the ordinary rust-cement (made of iron borings, sulphur, and sal-ammoniac) can be employed. In lieu of this another cement may be used, which is as tight, but is more easily removed. It is made by slaking lime to a powder, which is sifted and then kneaded with a little water to a stiff dough-like putty. This lime-putty is stemmed into the joints, hardens in 24 hours, and is perfectly tight against water and oils, either liquid or in the state of vapour; nor does heat affect it; only it must not be exposed to direct fire. For joining flanges, asbestos packing is no doubt the best possible material.

Instead of a condensing-worm, some works employ a double cylinder with a current of water in the annular space between the cylinders. Such a contrivance is evidently secure from being stopped-up.

The condensing-pipe is slightly bent upward where it leaves the tank (Fig. 101 at a); and at this place an upright pipe (b) is fixed, through which the permanent gases escape, whilst the liquid products run into the receivers. We shall see later on that the escaping gases ought not to pass directly into the atmosphere, but first through some purifying-apparatus.

Sometimes the bottom end of the condensing-pipe is fitted with a two-way or three-way cock, for changing the receivers and for conducting the contents of the still, in case of its boiling over, back into the tar vat. These aims are, however, better attained by means of the separating-box, shown below. We cannot recommend using a tap in this place (at the end of

the cooling worm), as it is too easily plugged up by solidifying naphthalene, etc.

Ellison and Davis (B. P. No. 13929, of 1886) employ the condensing-heat of the vapours for heating-up another charge of tar. In lieu of an open cooling-tank they employ a still

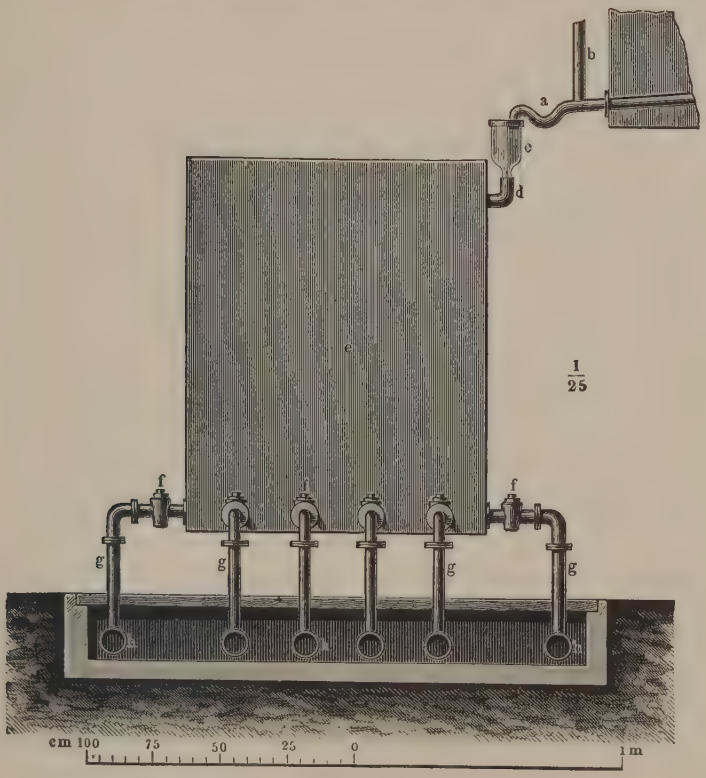


FIG. 101.

placed at a higher level with a worm into which the vapours from the tar-still are introduced at the top, whilst its bottom is connected with an ordinary cooler. When the distillation is finished and the pitch run off, the heated tar from the upper still is run into the tar-still proper and is distilled there as usual. The vapours escaping from the top still are of course condensed.

A similar plan has been patented by Max Böhm & Co. (Ger. P. No. 60747). We shall meet with the same principle in various patents to be mentioned later on. Gröling and Estlander (Ger. P. 98928) describe a special kind of heating-up apparatus, serving as dephlegmator for the gases from the still.

In order to separate the different products, there must be a corresponding number of *receivers*, and the products running out of *a* must be run at discretion into any of these. Many contrivances may evidently serve for changing the receivers; but some points must be always observed. Thus the receivers for the first products should be tightly closed, to avoid both loss and danger of fire. Furthermore, the first receiver must be provided with some contrivance for easily separating the oily and watery portions. The receivers for carbolic oil and those for heavy oils should be easily accessible, in order to remove the crystalline masses always separating in them. Above all, it is imperative to take every possible precaution against fire. If the receivers are placed near the tar-stills, they must be separated from them by a solid wall. Any tar which might by accident boil over and run out of the receivers must under no circumstances be allowed to get near the still-fires or any other fireplaces. At some places the receivers are only just large enough to hold the product of one operation. This has the advantage that the manager can judge of the still-work by the depth of the liquor in the receivers; but then there must be another and larger set of store-tanks for each fraction. Hence the receivers are frequently at the outset so constructed as to contain a large quantity of products, in which case they are placed at some distance from the stills and serve for a number of these at the same time.

Instead of dwelling upon the various ways in which receivers can be arranged, we prefer describing a special arrangement found at some of the largest works, and fulfilling the conditions of cleanliness, convenience, and safety. The distillates of each still run from the swan-neck pipe *a* (Fig. 101) into the glass jar *c*, in which the process can be well observed. A jar with hydrometer can be placed in it; samples may be taken from it; the rate of distillation is easily observed; the appearance of the products is noted, etc. When the oils become too hot, it can be replaced by an iron funnel. The glass jar *c* is closed by

a sheet-iron cover, with a hole for the passage of the pipe *a*. It is fixed into an elbow pipe, *d*, which conveys the liquids into the tight *separating-box e*. To this are attached as many cocks (*f f*) as there are different fractions to collect. These are simple 2-in. gas-cocks, made of cast-iron; brass cannot be employed, on account of the ammoniacal liquor. The cocks for creosote oil and anthracene oil may be larger, say 3-in or 4-in. bore. The cocks *f f* (in our diagram there are six) are connected by flanges with the pipes *g g*, which form vertical branches of the main pipes *h h*. The latter are laid in a bricked pit running along the whole set of stills, so that the products from all the stills pass into these pipes, which convey them ultimately into the store-tanks for each fraction. Care must be taken that the pipes *h h* have sufficient fall, and that the later distillates are not too much cooled in them, which would be sure to stop them up with naphthalene, etc. Such cooling is partly prevented by covering the pit over with planks; but it is safer to put steam-pipes into the pipes conveying the later distillates. A special cock in the bottom of the collecting-box *e* permits samples to be taken and the contents to be run off at will. It is also possible to adapt this box to a continuous separation of the ammoniacal liquor; but this is an unnecessary complication, and it is more advisable to let this separation take place in the receivers. One of the cocks must be connected with a pipe leading back into the tar-pits, or into a special small tank, to receive the tar when the still is boiling over.

A similar arrangement is shown by Engler (*loc. cit.*), and is represented in Fig. 102. The oil and water run through *a* into the cylinder A, where they separate. The water runs off through *b*; the gases escape through *c*; the oil runs through *d* into the "lantern" B, where the glass pane permits observing its colour, etc. From this point the oils are carried on through the taps 1 to 5 to the different receivers; the last, and heaviest, oils do not pass through the lantern, but straight into No. 5 through the tap d_1. This apparatus, which is used in refining petroleum, would require some modifications if it were to serve for distilling coal-tar.

The *receivers* or *store-tanks* for the various fractions may be of any shape—square, cylindrical, etc. They are always made

of wrought-iron, and should be very well riveted and caulked; otherwise, especially if placed on the ground or even underground, great losses by leakage may occur before anything is noticed, which may even seriously contaminate neighbouring wells and watercourses. Even a previous testing with water will only reveal coarser leaks, as tar-oils penetrate much more easily through the joints than water. Hence the store-tanks must be closely observed for some time; if they are sunk in the ground there must be a free space left all round them for some days after they have been first taken into use, so that any leaks may be detected and stopped before the earth is filled in. The bottom of the vessels ought always to be formed of one

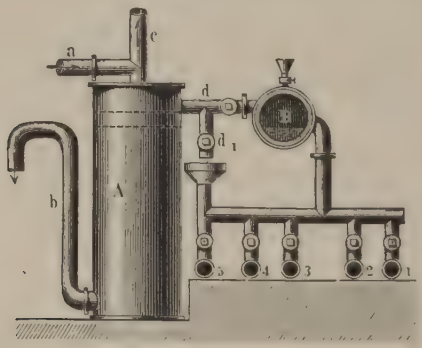


FIG. 102.

piece. Of course the needful precautions against corrosion by rusting must be taken.

Light oils are best kept in closed cylinders, heavy oils in open tanks, from which the solid naphthalene or anthracene crystallizing out can be easily removed.

At some works, steamboiler-shaped cylinders (either horizontal or upright), which can be also used for *forcing-up the oils by air-pressure* (*montejus*), are preferred as receivers, or at least as store-tanks. Instead of pumping the liquids by means of ordinary pumps, which is very inconvenient with tar-oils, owing to the impossibility of employing fatty or indiarubber packings, they are now nearly always pumped by air-pressure, compressed air being conveyed from an air-pump or blowing-engine to each of the receivers. This air presses on the

surface of the oil and forces the liquids through ascending pipes, which reach down to the bottom of the vessel, and are provided with stopcocks, to any suitable height or place. Hence the moving parts of the machinery are nowhere in contact with the oils.

Treatment of the Gases escaping from the Condensers.

We have already mentioned the permanent gases formed in the distilling process. They are partly combustible; but it will hardly ever pay to utilize them in this respect, especially as that would entail considerable danger of fire. However much cooled, these gases at first carry away some of the most volatile of the tar-oils mechanically. Moreover, they contain sulphuretted hydrogen, ammonium sulphide, carbon bisulphide, perhaps carbon oxysulphide, and other noxious gases, which may at times give rise to complaints of nuisance. Detailed observations on this subject are described in the *Alkali Inspector's Report for* 1897, p. 35. So long as the distillate contains water, there is but little H_2S in the gases, the smell of CS_2 and of NH_3 predominating. When the water ceases to appear, the smell of H_2S increases, and later on the gases have much heating-power. Towards the end of the process vapours of a very offensive and irritating kind are evolved, which are not completely condensed. Hence it will sometimes be necessary to subject the gases to a purifying process. An apparatus for this purpose, substantially as employed at a large London tar-works, is shown in Figs. 103 and 104. The gas-pipes of all the cooling-worms are connected with a main pipe, which ultimately descends at *a* and enters the box *b c*. This is divided into two parts by a partition, *d*, which does not reach quite to the bottom. The compartment *b* is empty, with the exception of a little water at the bottom, which is kept level with the lower edge of the partition *d* by means of the overflow-pipe *e*. The compartment *c* is filled with coke or some other material presenting a large surface, and constantly moistened with water by means of the perforated cross-pipe *f*. This compartment serves as a scrubber: the gas is washed by the water; and at the same time the oily parts are condensed, owing to the speed of the gases slackening; the friction upon the surface of the coke, and the rinsing action of the water. It seems preferable to assist the division of the gas into many jets

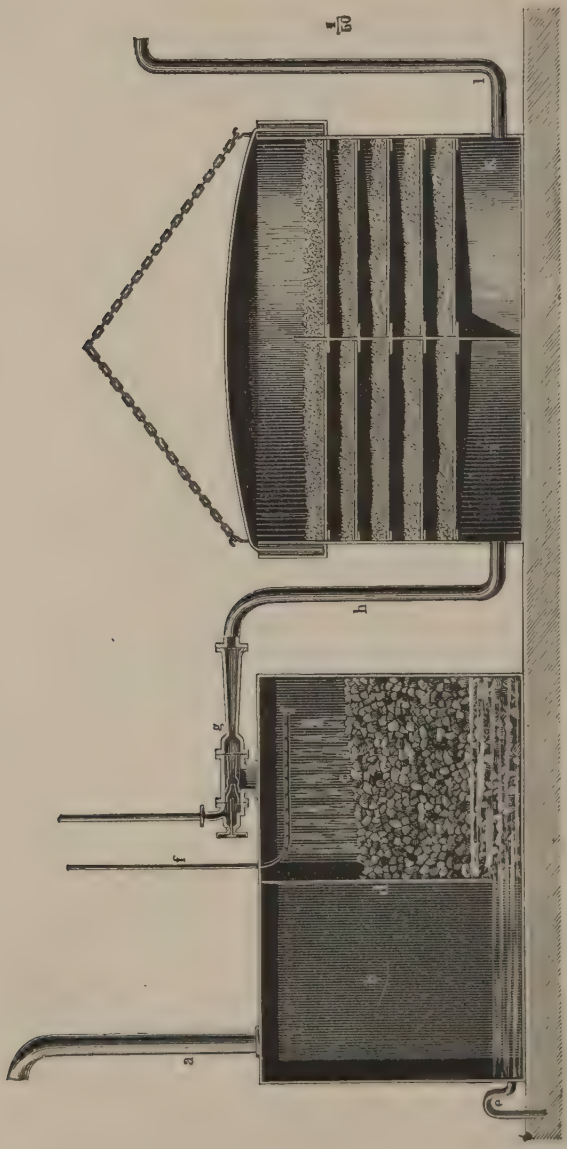


FIG. 103.

by nicking out the lower edge of the partition, *d*, as shown in Fig. 104. In most cases the gas will be allowed to escape by means of a pipe put on the top of *c*, either into the open air or into a chimney; only provision must be made for preventing the water in *b* from rising quite up to the partition *d*, so that the gas can pass through. But where it is desirable to prove to the public that no precaution against nuisance has been neglected, a further purifying-apparatus is added, say an oxide-of-iron purifier (*i k*), from which the gas escapes at *l* into a chimney-flue. This purifier is exactly like those used at the gas-works, but on a much smaller scale. If the washing in *c* is to be made especially good, the gas is forced right through the

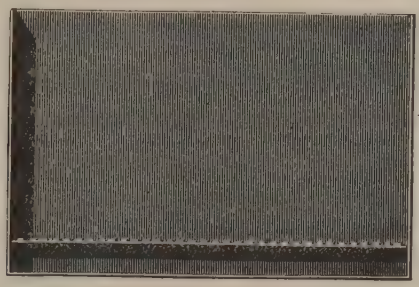


FIG. 104.

water by means of an injector (*g*), which takes it through *h* to *i*. The liquid hydrocarbons are all retained in the vessel *b c*; the sulphuretted hydrogen is absorbed in the purifier *i k*; and the last remnant of the smelling gases is made innocuous in the hot fire-flue into which it passes.

Another arrangement for avoiding all nuisance, by the use of a vacuum, as devised by Mr S. B. Boulton, will be described later on, when treating of the vacuum process.

According to the *Alkali Reports*, 1893, p. 20, the gases can be aspirated from the end of the worm by an injector or fan-blast, and passed through a water-lute into a fireplace, or else underneath a grating placed in a brick-pit, oxide of iron being put on top of the grate.

If (as happens sometimes) one set of condensers acts for two or three stills, there is a possibility of noxious gases getting from this condenser into an empty still which men are busy

cleaning. They might be suffocated thereby, and that arrangement must be, therefore, altogether condemned.

Rambousek, in the ninth volume of the *Zeitschrift für Gewerbe-Hygiene*, published at Vienna, reports on the injurious action of those gases on the respiratory organs, and on the "tar- and paraffin-itch" or "acne" caused by the action of the tar.

A very important paper on the noxious vapours from tar-distillation is that of Craven and Coleman.[1] We quote the most salient points of it. Of the various gases escaping at the end of the condensing plant, the sulphuretted hydrogen is that which is most easily subjected to accurate estimation, and it is probably also the most important in the question of "nuisance." It appears at two periods; in the beginning, where from 5 to 10 g. H_2S per cubic foot is present, and again from the commencement of the light-oil stage up to the end; during this time its proportion regularly increases, beginning with 10 and ending with 112 g. per cubic foot. The most usual way of dealing with it (where this is attempted at all) is to draw it through a water-seal and then pass it underneath a fire, mostly the steam-boiler fire. Even if all H_2S is burnt here (which is frequently not the case), it is converted into another noxious gas, viz., SO_2; this may injure the boiler plates, and sometimes explosions have occurred from this cause, when the action of the aspirator was disturbed in some way, and the fire flashed back through the water-seal. This method, therefore, ought to be entirely abandoned. Another, much practised, method is the application of absorbing media in "dry purifiers" (*vide supra*, p. 351). When employed in the ordinary manner, drawbacks are caused in this process principally by the action of the carbon bisulphide. The authors therefore attempted to solve the task by the employment of "wet purifiers." They force the gas by means of an air-pump (which they prefer to an exhauster as being more reliable) through an absorber, charged with milk of lime and sulphate of iron, and therefore containing hydrated oxide of iron, and after distilling each batch of 40 tons tar, they pump air through the absorber during an hour, which is quite sufficient for revivifying the absorbing agent. Of course this becomes gradually inactive, but experience has shown that 1 cwt.

[1] *J. Soc. Chem. Ind.*, 1901, p. 200.

of lime and 2 cwt. of sulphate of iron in 200 to 300 gall. of water suffice for about 400 tons of tar. The gas issuing from the absorber has a slight odour, caused by hydrocarbons, which might be dealt with by a second absorber, charged with heavy tar-oil. For a complete plant they propose to send the gases first to a coke scrubber, where a very small stream of water would absorb the ammonia, then through an absorber fed with high-boiling tar-oil, where carbon bisulphide and hydrocarbons would be retained, then through an absorber containing a mixture of water, sulphate of iron and lime, and at last through another absorber, containing the same mixture, or else milk of lime only. The pump, of course, is placed at the end of the whole set. Sometimes free sulphur is deposited in front of the coke scrubber, which can be dealt with before the gases reach the scrubber.

When this paper was published, there had not been sufficient experience gained to declare the process as absolutely successful in all respects, but it seems the best as yet proposed.

Working of the Tar-stills.

The stills are *charged* with fresh tar while they are still hot from the last operation, but not so hot that they might suffer damage from the cold tar—that is, a few hours after running off the pitch. The tar is either pumped in directly or run in from a higher tank previously filled. In both cases the bore of the feed-pipe is wide enough for the charging not to take too much time, say 6 ins.; the air escapes not only through the condensing-worm, but also by an air-cock or by the overflow-cock, *s*, Fig. 88, p. 332. The latter also makes any other gauging of the contents of the still unnecessary. Where it is absent, the level of the tar must be ascertained by a float, or by a gauge-rod introduced into a hole, afterwards closed by a screw-plug. The stills may be filled up to the point where the cylindrical part merges into the dome-shaped portion. Watson Smith states the permissible level at 9 to 12 ins. below the manhole—with thin tars, 18 ins. below the same. This is not a sufficient indication, as the manhole is not always placed at the same height. We may better state the case thus: that the space between the overflow-cock and the still-top should be 24 to 30 ins., and in semi-globular domes 36 ins.

All the openings are now closed and the firing is commenced. The *heating-up* may even be begun when the still is only half filled, as the level of the tar is then above the flues; although the air-cock or overflow-cock is then open, no loss is incurred, because the heating-up of the large bulk of tar takes much time, and the new tar running in causes a constant cooling. Care must be taken to see that the worm is not choked up, which sometimes happens in this way; after the close of the previous operation the distillation slowly continues, whilst the water in the condensing-cistern cools down, so that "green grease" accumulates in the worm; this can usually be cleared out by blowing steam through the worm. At some works the state of the worm is tested by running a little water through it before commencing the work. As soon as the charge is all in the still and the openings are closed, the fire is increased; and this is continued up to the point at which distillation is about to commence. This will occupy more or less time, according to the size of the still and the season; with small stills (5-ton charge) it requires about two hours, with large ones (20- to 25-ton charge) it takes five hours in summer, six hours in winter. One or two hours after the commencement of firing, the tar begins to rise and froth; and now the greater part of the ammoniacal liquor can be run off by the overflow-cock. After this the firing must take place somewhat more cautiously, to avoid sudden boiling-over, which might otherwise happen with the violence of an explosion. From this time up to the beginning of the distillation the fireman should always be in his place and must watch the worm. As soon as the first drops appear at the end of the refrigerator, he must open the fire-door and slacken the fire; for now the danger of *boiling-over* is greatest. With proper management of the still this need *never* occur (excepting the case of tars containing too much water, which ought to be previously removed, as shown p. 314, or too much free carbon, see next page); but if it does take place it is little use opening the fire-door, letting down the damper, etc., because the mass of heat stored up in the tar, the iron, and the brickwork is too great; even completely drawing out the fire (which can only be done if the still is quite isolated) does not act instantaneously. But it does good to pour cold water on to the still-top; and the same means must be resorted to

whenever for any reason the distillation is to be stopped as quickly as possible. When working with properly dehydrated tar none of these precautions will be needed, and much time is saved as well.

The following are signs that distillation is about to begin :— Vapours issue from the end of the cooling-pipe, often in puffs, and gradually drops are condensed from them. The still-head gets warm, and the worm also where it is not yet covered by the cooling-water. Now in any case the fire must be slackened ; for the distillation will commence directly. This is still more necessary as soon as a continuous jet of liquid comes out of the worm ; it is then time to open the fire-door, or, what is better, to let down the damper. If at this stage there is any excess of heating, the ebullition takes place with violent bumping and frothing-up, and in the worst case the mass suddenly swells up and boils over. The tendency to eruptive ebullition was formerly attributed entirely to the *water* contained in the tar, and was believed to be all the greater the more water is present. It has already been mentioned how the quantity of water, and with it the bumping and frothing, can be diminished.

Köhler (*Z. angew. Chem.*, 1888, p. 677) states that the boiling-over of tar-stills is in the majority of cases caused by an excessive percentage of *free carbon*, which causes the vesicles of gas and vapour to adhere to the carbon particles, and thus greatly swells the volume of the tar. Whilst tars with 12 or 15 per cent. free carbon, even when containing much water, distil quite normally, other tars containing 20 to 28 per cent. free carbon show a strong tendency to boil over. Kraemer (priv. comm.) entirely objects to this opinion ; tar rich in carbon retains the water more pertinaciously, and is separated from it less easily. The presence of *gases dissolved in the tar* also increases that tendency.

The following proposals have been made for preventing the boiling-over of tar-stills. Luhmann places below the outlet-pipe a lenticular wrought-iron vessel (Fig. 105), provided with an outlet-pipe carried outward, and a pipe connecting its top with a water-reservoir. When the attendant notices a swelling-up of the tar, he should open the water-tap ; the top part of the still is thereby cooled, and the condensing liquid, raining down upon the boiling tar, breaks up the froth. Later on Schroeder

patented the same arrangement (Ger. P. 76366). H. Kropff (Ger. P. 55933) removes the froth by blowing cold air on to the surface of the boiling liquid.

Le Clercq's Patent Gesellschaft zur Fabrikation von Teer- und Dachpappen-Maschinen (Ger. P. 166723) describe a system, claimed to be safe against fires and boiling over. A system of heating-coils, a closed tank, and a pump are connected in such manner that only the contents of the coil can get into direct contact with the fireplace, thus enabling the heating of the tar, without danger of fire, to much higher temperatures than is otherwise possible.

During the first period of the distillation permanent gases, water (containing ammonium compounds), and the most volatile tar-oils are given off, which always carry along some of the less volatile constituents, partly in consequence of the vapour-tension

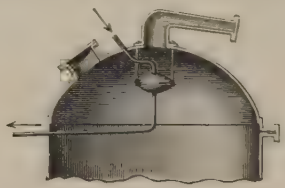


Fig. 105.

of the latter, partly mechanically. During this period the cooling-tank must be well supplied with cold water, both for condensing the tar-oils and because the condensation of the steam and ammonia liberates much heat. A 1-in. water-pipe and 15-ft. head of water will supply a cooling-tank for a 20-ton still.

Most frequently the *first fraction* is that portion of the oils which comes over along with water; so that the first receiver contains both ammoniacal liquor and tar-oils. The latter are called first runnings, first light oils, crude naphtha, etc. Water will form a greater or smaller proportion of the distillate, according to whether it has been previously removed or not; this proportion is ascertained by catching some of the distillate in a glass cylinder, in which naphtha and water separate at once, the former floating on top of the water. At first much water and little oil comes, then less water and more oil;

occasionally the time when the water ceases to come over can be somewhat accurately fixed for changing the receiver. But it is safer to wait till the distillation slackens. This is called the "break," and is probably caused by the fact that the aqueous vapour carries along a quantity of oils of much higher boiling-point than that of water; so that, after all, the water is removed first. The temperature has to rise a good deal before the liquid begins to boil anew. At this stage, often for two hours, hardly anything comes over but a little water; and, from the peculiar noise made by the steam within the still, this period is sometimes called the "rattles." The cause of the rattles is the falling-back into the contents of the still of the last portions of water which had been vaporized and had been condensed before getting into the worm. When coming in contact with the tar, now heated considerably over 100°, it is instantaneously re-vaporized with a somewhat explosive force, and thus the rattling or crackling sound is produced. The same phenomenon is often observed when distilling, in the laboratory, naphtha containing traces of moisture. The rattling noise ceases when the temperature has risen high enough; and the distillate then comes over in a thick, quiet stream. It is now mostly collected in another receiver as "light oil" or "second light oils."

The ceasing of the appearance of water is not by itself a sufficient signal for changing the receiver; for sometimes a little water comes off along with the light oil, and even, at first, with the heavy oil, from the hydration water of phenol. Hence other signals must be the smell, the specific gravity, and the quantity of the distillate, or else the indications of the thermometer. The smell, which of course cannot be very well defined, generally indicates to the attendant quite clearly when he must change the receiver for light oil: the first runnings smell much more pungent than the light oil; and the transition is pretty sharp. The specific gravity increases slowly, and does not in this case give very distinct guidance.

Of course the specific gravities of the various oils must not be compared at different temperatures, but must be reduced to the ordinary temperature, *e.g.*, by placing the hydrometer vessel (which for factory purposes is best a *lead* cylinder, not a glass jar) into a bucket with cold water, until the temperature has

gone down to 20° C., which in the warm season takes some time. To save this, Peterson-Kinberg gives the following table, showing the specific gravities at various degrees C. :—

80°	70°	60°	50°	40°	30°	20°
...	...	0·96	0·97	0·98	0·99	1·00
...	...	0·987	0·998	1·009	1·019	1·029
...	1·005	1·013	1·018	1·025	1·035	1·045
1·01	1·02	1·03	1·038	1·05	1·06	1·07
1·02	1·03	1·04	1·048	1·06	1·07	1·08

If the fractions are to be made according to the indications of the thermometer fixed in the still (p. 338), it is usual to change at the following points:—

1. First runnings, up to 105° or 110° C.
2. Light oil, up to 210°.
3. Carbolic oil (for phenol and naphthalene), up to 240°.
4. Creosote oil, up to 270°.
5. Anthracene oil, above 270°.

These points are, of course, not always the same, partly because the thermometers do not reach down exactly to the same depth. Thus a large German works changes as follows:—

1. Light oils, up to 165° or 170°.
2. Middle oils (for carbolic acid and naphthalene), up to 230°.
3. Creosote oil, up to 270°.
4. Anthracene oil, above 270°.

Girard and Delaire (*loc. cit.*, p. 10) quote the following fractions:—

1. Huiles légères,	from	30°	to	140°,	sp. gr.	0·780	to 0·850
2. Huiles moyennes,	„	150°	„	210°,	„	0·830	„ 0·890
3. Huiles lourdes,	„	220°	„	350°	„	0·920	„ 0·930

(The specific gravities are evidently wrong, and, no doubt, again prove an unaccountable confusion with paraffin oils.)

The following special observations have been made by H. Köhler with a 15-ton still, worked in a regular way up to medium-hard pitch, with a vacuum. The specific gravities were

taken at 15° C. for the lighter fractions, at 30° C. from carbolic oil upwards. The tar distilled weighed 15,000 kgs.

Time of sampling.	Temp. in the still-head.	Ammoniacal liquor.		Oil.		Quality of distillate.	Total quantity of distillates.
		Volume per cent.	Specific gravity.	Volume per cent.	Specific gravity.		
	° C.						
8 A.M.	80	40	1·080	60	0·878	First runnings.	880 kilog. aqueous liquor; 440 kilog. oil; sp. gr. 0·925.
10 ,,	92	57	1·020	43	0·891		
12 NOON.	95	60	0·990	40	0·892		
2 P.M.	96	63	0·995	37	0·893		
4 ,,	97	65	0·996	35	0·897		
6 ,,	97	70	0·999	30	0·901		
8 ,,	98	80	1·000	20	0·902		
10 ,,	98	75	1·000	25	0·905		
12 MIDN.	98·5	70	1·000	30	0·905		
2 A.M.	98	70	1·000	30	0·910		
4 ,,	98	65	1·000	35	0·917		
6 ,,	98	60	1·002	40	0·922		
8 ,,	98	50	1·005	50	0·923		
10 ,,	98	30	1·050	70	0·950		
10.30 ,,	167	6	1·095	94	0·960	Light oil.	250 kilog.; sp. gr. 0·995.
11 ,,	220	...	...	100	0·980		
11.30 ,,	223	...	...	100	1·000		
12 NOON.	230	...	...	100	1·010	Carbolic oil.	520 kilog.; sp. gr. 1·015.
12.30 P.M.	239	...	...	100	1·015		
1 ,,	240	...	...	100	1·023		
1.30 ,,	252	...	...	100	1·025		
2 ,,	255	...	...	100	1·029	Creosote oil.	1800 kilog.; sp. gr. 1·045.
2.30 ,,	263	...	...	100	1·035		
3 ,,	265	...	...	100	1·040		
3.30 ,,	269	...	...	100	1·049		
4 ,,	278	...	...	100	1·057		
4.30 ,,	280	...	...	100	1·065		
5 ,,	285	...	...	100	1·086	Anthracene oil.	1450 kilog.; sp. gr. 1·095.
5.30 ,,	285	...	...	100	1·095		
6 ,,	290	...	...	100	1·099		
6.30 ,,	285	...	...	100	1·0995		

In the case of tars of known quality, the time and the quantity of the distillate are among the most important signals for changing the receivers. The former varies of course with the size and even with the shape of the still, its setting, etc. We shall make some statements regarding this subject and the quantity of the different fractions at the end of this chapter. The quantity of the distillate can only serve as a guide where each still has its own receivers, which is rarely the case at large works.

Attempts have been made to greatly increase the number

of fractions at the first distillation of coal-tar, with the view of better isolating the products therefrom. All such attempts have hitherto failed, and probably will continue to do so in future. In no case are pure products obtained, and hardly any of the subsequent rectifications are saved; so that the whole is but a superfluous complication of the process. This is founded on *the nature of fractional distillation*, which has only recently been cleared up by a number of researches.[1]

The various components of a mixture do not distil simply in the order of their boiling-points, not even taking into account the vapour-tension of the substances not yet arrived at their boiling-point; but their vapour-density must also be taken into account. According to Dossios and Wanklyn, the quantity of each component distilling at a certain temperature is found by multiplying its vapour-tension at the boiling-point of the mixture by its vapour-density, or, what comes to the same thing, its molecular weight. Thus methylic alcohol (molecular weight = 32) boils at 66°, methylic iodide (molecular weight = 142) at 72°; but from a mixture of the two, more of the latter distils over. A mixture of 91 parts carbon bisulphide (boiling-point 47°) and 9 parts alcohol (boiling-point 78°) boils constantly at 43° to 44°, and during distillation retains its composition. Hence the liquid possessing the highest vapour-tension does not necessarily distil most rapidly; for what its companions lack in tension they may make up in vapour-density. If the tension is called t, the vapour-density d, we have for different liquids $x = ktd$, in which formula k is a constant to be found by experiment in each single case. If the vapour-densities and tensions are inversely proportional to each other, and the values of k are equal, the products $k_n t_n d_n$ will all be the same; *i.e.*, the mixture will remain unchanged throughout the distillation. For this reason homologous series (*i.e.*, those whose members differ from each other by CH_2) are not easily separated by fractionating; for whilst the vapour-tension is lowered by each CH_2, the vapour-density rises. This explains why so many substances distil more quickly in a current of steam; for aqueous vapour

[1] Dossios, *Jahresber. f. Chem.*, 1867, p. 92; Wanklyn, *Phil. Mag.* (4) xlv., p. 129; Glashan, *ibid.*, p. 273; Naumann (*cf.* below); Thorpe, *J. Chem. Soc.*, 1879, xxxv., p. 544; F. D. Brown, *ibid.*, p. 547; 1881, xxxix., p. 304; Konovalow, *Ber.*, 1881, pp. 2224 and 2678, etc.

is one of the lightest bodies. By diminishing the pressure the difference between the vapour-tensions of different liquids is increased, whilst their vapour-densities remain the same;[1] hence, according to some, they are more easily separated, as is proved by the success of exhaustion in gas-making and tar-distilling (see below). But to this it has been objected that the lowering of the boiling-points, caused by producing a more or less complete vacuum, does not in reality facilitate the separation of the various fractions, the differences in their boiling-points remaining practically unaltered.

A *mixture of two liquids which are not mutually soluble*, on distillation, exhibits a boiling-point below that of the more volatile substance. A mixture of carbon bisulphide (boiling-point 47°) and water boils at 43°, etc. This observation has been generalized by Naumann,[2] who found that the boiling-point of such a mixture is constantly below that of the most volatile component,—and also that the proportion of substance is always the same, viz., equal to the proportion of the vapour-tensions of the two components, measured at the temperature of boiling, multiplied by their molecular weight. This behaviour is of importance to us in tar-distilling also, where water boils in presence of oils not miscible with it. Thus, although at 98° the vapour-tension of naphthalene is only 20 mm., that of water 712 mm., yet at that temperature 49·4 g. of water pass over with 8·9 g. of naphthalene.

It is hardly necessary to mention that the different fractions are not divided by any sharp lines, and that at different works they are taken differently. In some places no distinction is made between first runnings and light oils, but all that has a specific gravity below 1·0 is taken as crude naphtha. The subsequent treatment must be adapted to this.

First fraction.

In any case *first runnings* and (aqueous) *ammoniacal liquor* come together, the former floating on the latter. The latter is worked up like any other similar liquor, as will be described in the latter part of this book. The two liquids at once separate sharply; the water is either pumped away from below, or is

[1] Winkelmann, *Poggend. Annal.*, N.F., i., p. 430.
[2] *Ber.*, 1877, p. 1421; 1879, pp. 2014, 2099.

continuously carried away by a pipe starting from the bottom of the receiver, and turned upward; or else the same object is attained by a partition reaching nearly to the bottom of the receiver, or in any other way.

Light Oil.

The *second fraction* (if the distillate coming over before the carbolic oil is, as usual, divided into two fractions) begins after the "break," when the distillation proceeds quite smoothly, in a full stream and without any further danger of boiling over. The product is no longer a naphtha, but has a more oily nature; it is called either "light oil" or else "second light oil," or "second runnings." We shall in future use the first name in this restricted sense. This fraction is usually continued up to the point where its specific gravity is equal to that of water, The men run a few drops into a cylinder partly filled with water; if the oil floats anywhere within the water in single large, globular drops, its specific gravity is $= 1.0$, and it is now time to change the receiver for carbolic oil. Where the fractions are made by the thermometer, this point will be about 210°. This proves that the light oil must contain a good deal of carbolic acid (boiling-point 180°) and naphthalene (boiling-point 218°); but it must be remembered that in the upper part of the still and in the still-head some cooling takes place and the vapours partly condense again; hence the principal part, especially of naphthalene, only comes with the next fraction. But where carbolic acid and naphthalene are principal considerations, the fractionation is managed accordingly. This is the object of the method of working mentioned on p. 360, where the "middle oil," passing over between 165° or 170° and 230° will comprise nearly all the phenol and naphthalene, especially if the bulb of the thermometer is not placed in the tar, but in the liquid.

Another signal, sometimes used, for changing from light oil to the next fraction is obtained by letting a few drops of the distillate fall upon a piece of cold iron. If a crystallization of naphthalene sets in, it is time for changing. But this holds good only where no "carbolic oil" is separately received.

During the time the light oil is coming over (that is, after the "break"), the fire is increased without any danger of boiling

over, although even now for the most part a little water appears, probably owing to the hydrate of phenol splitting up. Now the cooling-water begins to get warm; but little or no fresh water is run in; so that at the end of this stage the temperature of the water surrounding the worm is about 40°. If the work is arranged for "middle oil" in the above-mentioned sense, the water must be at least from 50° to 60°. Afterwards no fresh water at all must be run in; and sometimes even steam must be blown into the cooling-tank by means of a pipe entering at its *bottom* and pierced with numerous holes (*b*, Fig. 95, p. 343): this is necessary because the danger of the worm being choked up is greatest in the bottom coils. Such a danger sets in even more near the end of the process, as we shall see later on; but it can always be provided against by allowing the water to get hot. Some English tar-distillers have not even steam-pipes in their refrigerators; but this is advisable in any case.

If the temperature in the refrigerator were kept too low, in the later period of the light-oil stage the naphthalene would crystallize and choke up the worm, thus producing a dangerous pressure in the still. The explosions of tar-stills, seldom as they occur, are probably always caused by neglect in this respect, either during the naphthalene- or the anthracene-period.[1] On the other hand, the water should not be allowed to get warm at the beginning of the light-oil stage, because then considerable quantities of the more volatile hydrocarbons are still coming over. This seems to be another reason for continuing the first fraction till benzene and all its homologues have passed over, and then condensing the "middle oil" with warm cooling-water.

Whether the worm is choked up, or not, is best seen at the end of the pipe coming out of the refrigerator, where it is curved up to allow the permanent gases to be taken away. This pipe should be warm, and the liquid should run out uninterruptedly: this is readily seen when it runs into a glass jar (*c*, Fig. 101, p. 347). Where there is an intermediate vessel (*e*, Fig. 101) with cocks for the different fractions, the distillate might possibly crystallize in this, or in the pipes (*g g*) that carry away the

[1] A frightful explosion occurred in this way at a tar-works near Gateshead-on-Tyne, in 1886, by which several people were killed, among them the managing partner. The tar-stills were not provided with safety-valves.

products. This is not so very dangerous, because the whole box *e* must be first filled with crystals before the worm can be choked up; notice will be given of it by the box *e* or the cocks *f* getting cold. If the pipes *h* are sunk in the ground, are covered up, and have sufficient fall and are not too long, they will not be easily stopped up; but it is decidedly advisable to be prepared for that contingency by making provision for blowing steam through them.

Where the work is carried on with evacuation by an air-pump or an injector, in the manner to be described hereafter, there is absolutely no danger of any choking-up of the worm. But in any case the stills ought to be provided with a safety-valve or an equivalent contrivance (p. 337).

J. Vaughan[1] proposes preventing explosions that might occur, in consequence of the worm choking-up, by means of a wide pipe reaching nearly to the bottom and passing out at the top, connected with a large empty cylindrical boiler placed near the still and at a lower level. The connecting pipe is enlarged at the highest point, and is there closed by a valve kept down by its own weight. The whole of the pipe is kept warm. If any excessive tension should occur within the still, the tar will rise in the pipe, lift the valve, and flow over into the empty cylinder. This is evidently exactly the same method as that practised in Germany many years ago (p. 336).

Carbolic Oil.

The distillate at and above the specific gravity 1·0 was formerly not fractionated at all, but collected all together as heavy oil, dead oil, or creosote oil, and sold for pickling timber, without any further manipulation. Only exceptionally could the first and the last portion of the creosote oil be separately sold, the former for carbolic acid, the latter for lubricating-grease. When carbolic acid was aimed at, there was but rarely a special fraction made for it; the light oil was only driven a little further. No doubt phenol and its homologues, as we shall see in Chapter IX., occur also further on in the heavy oil, and constitute part of its value for preserving wood; but making pure phenol from proper heavy oil is rather

[1] *Engineer*, 1880, v., p. 298.

difficult and expensive, and only takes place exceptionally. For this reason, since large quantities of phenol have been required for the manufacture of colours, for disinfecting, and for medicinal purposes, it has become usual to make a special fraction containing as much carbolic acid as possible and with it a great deal of naphthalene. Although the boiling-points of these compounds are wide apart (180° and 218°), a large quantity of naphthalene is carried over below its boiling-point, and, on the other hand, phenol is kept back in the tar-oils above its boiling-point. Where no thermometer is placed in the tar-stills, this fraction is made to commence whenever the specific gravity of the distillate is 1·0; moreover, its yellower colour and its smell serve as guides. A certain quantity of the oil now passing over is received as "carbolic oil"; and when this quantity has come over, the change for creosote oil is made. The amount of carbolic oil is usually 100 gallons from a charge of 2000 to 2500 gallons, *i.e.*, 4 or 5 per cent. of the tar. Ordinary Lancashire tar gives 5 per cent. by volume of good crude phenols, yielding 65 per cent. (by volume) of a carbolic acid, sufficiently pure to crystallize at ordinary temperatures with ease (Watson Smith, *J. Chem. Soc.*, 1886, vol. xlix., p. 21).

Where it is preferred to consult the thermometer, at some works the fraction passing over between 210° and 240° is taken as carbolic oil (probably the bulb of the thermometer dipped in the liquid itself), whilst at other (very large and well conducted) works the "middle oil" is received between 170° and 230. The latter course seems most worthy of being recommended, as it leaves a suitable margin below the boiling-point of phenol and above that of naphthalene. Where "prepared tar" for the manufacture of roofing-felt is made, it is usual to stop the distillation at 210°, and run the now remaining contents of the still into the receiver.

If the oils on cooling show a large crystallization of naphthalene, this is a sign that most of the phenol has already come before, or that it is now time to change for creosote oil; for naphthalene is much more soluble in phenols than in the heavy indifferent tar-oils, and hence mostly remains dissolved in the distillate so long as there are considerable quantities of phenols present, but crystallizes in large masses on cooling

when the phenols are becoming scanty; but this rule is not without exceptions.

Each factory must, of course, ascertain for itself which are the proper limits of this fraction; they will depend upon the size and contents of the stills, the position of the thermometer, the quantity of the tar, etc. The criterion is that the crude carbolic acid, obtained by the subsequent treatment of the carbolic oil, is of the proper quality, as will be explained in Chapter IX. So far as naphthalene is concerned, enough of it is sure to come over, and sometimes it crystallizes out in large quantities. Only exceptionally does tar contain so little naphthalene that it is not partly separated in the solid state. Hence the previously mentioned precautions for preventing the choking-up of the pipes should be always observed in this case.

Creosote Oil.

The fraction which comes over after the carbolic oil generally contains at first sufficient naphthalene for some of it to crystallize on cooling in a shallow dish. But after some time this ceases; the naphthalene, still present, but in smaller quantity, remains dissolved in the liquid hydrocarbons even after cooling; and as phenol and its homologues, which impart to the products the property of promoting friction, have ceased even before, the portions now received possess a milder, more oily or greasy nature, which makes them suitable for cart-grease. Hence this product is frequently called "soft oil," or "liquid creosote oil." It generally begins to appear when about half of the heavy oil (calculating for a distillation up to hard pitch) has been received. Before an industrial use had been found for the anthracene oil, the second half of the heavy oil, *i.e.*, the "soft soil," along with the "red oil," or anthracene oil, was sometimes run into a special receiver as "grease oil," and the liquid soft oil was occasionally separated from the butter-like grease. This was done chiefly in the first years after 1860, when, owing to the American civil war, the price of rosin had risen enormously, and the cart-grease-makers were glad to get any substitutes for rosin-oil; and this is now again done at some tar-works. The liquid soft oil is often called "yellow creosote," from its yellowish-green colour,

which, however, soon changes into dark brown. Its value as a lubricant is inferior to that of the last portion, the "solid creosote," or a green grease answering to what is now called "anthracene oil." In any case these products are very much inferior as lubricants to rosin-oil or lubricating oils from petroleum and paraffin-oil refineries. The separation of yellow from solid creosote is now principally made for the purpose of obtaining, in the "*anthracene oil*," that constituent of coal-tar (viz. anthracene) which, since Graebe and Liebermann's discovery of artificial alizarin (1868), has become by far the most valuable product of this industry. All the remaining heavy oils are put to the uses described in Chapter VIII.

Since the tar made at the Scotch gas-works contains too little carbolic acid and anthracene to make it worth separating, most of the Scotch tar-distillers do not make the fraction here described, but collect all the heavy oils together for pickling timber.

Anthracene Oil.

The beginning of the anthracene-oil period is either judged by outward marks or by the thermometer, sometimes by the quantity of the distillate. Usually it is calculated that about one-sixth of the heavy oil (reckoning from sp. gr. 1·0 up to hard pitch) comes over as anthracene oil; but in some cases as much as one-half of the heavy oils is collected as anthracene oil. The latter may be reckoned to begin when the oil ceases to remain liquid after complete cooling—that is, when a fresh separation of solids sets in. Where the thermometer is employed, 270° is nearly everywhere assumed as the commencing-point. Probably this general consent results from the fact that from this stage the thermometer-bulb is always in the vapour. Sometimes first and second "green oil" or "red oil" are received separately.

End of the Distillation.

Formerly this was decided according to whether hard or soft pitch was to be left in the still. Sometimes, but rarely, the work was stopped as soon as all the light oil had passed over; the residue then remaining in the still was called "asphalt," and employed in the paving of streets, for protecting underground iron tanks from corrosion, and similar purposes (see

next chapter). But the work was nearly always continued further, either up to soft pitch or hard pitch (*brai gras* and *brai sec*). Soft pitch is obtained when rather more than half the dead oil is distilled off; moderately hard pitch, when the soft oil and the first portions of anthracene oil are taken away; hard pitch, when the distillation is carried to its conclusion, as will be described presently. The special characters of these different descriptions of pitch will be given in the next chapter.

Since anthracene has become the most valuable product of tar-distillation, wherever the tar is not very poor in anthracene, the distillation is mostly continued till hard pitch is produced. In England and France it is frequently run out in this state; but in many English and Scotch works, and in most or all German ones, they manage differently, as we shall see.

In the last period of the distillation the water-supply to the worm-tub should be shut off altogether, the water in the tub allowed to boil, and, if necessary, ebullition must be produced by blowing in steam.

The distillate which now separates is a mixture of anthracene, phenanthrene, carbazol, etc.; later on also of chrysene, pyrene, etc.; and ultimately contains so much of these that on cooling it solidifies in a butter-like mass which would choke up all the pipes. This must of course be avoided by keeping the worm-tub and the conveying-pipes warm, or even (more safely) by employing steam; but the best way of all is by producing a vacuum (see below). The oil running off should be about 60° C. If the distillation is continued till hard pitch is formed (*i.e.*, pitch which will be hard when cold), it becomes at last very sluggish; its cessation is determined by the manner in which the distillate solidifies and by its quantity—also by the time elapsed, and by the peculiar smell, now again changing. Steam being usually injected now (see below), the thermometer is of no further use; and in any case a mercurial thermometer could not be employed at this stage, the temperature in the interior of the still being 360° C. In the case of tars containing too little anthracene, etc., to solidify, the other signs must suffice for judging when to stop. Frequently, also, the hydrometer is consulted. If the distillate shows a specific gravity = 1·080 to 1·090, the residue will be moderately hard pitch; at 1·120 it will be hard pitch; but this does not hold good of all descriptions of coal-tar, and should be

tested by experiment. As soon as the distillate assumes a "gummy" state, the distillation should be stopped, for this product, although still containing anthracene, cannot be filtered at all. Under all circumstances the decisive criterion is the quantity of the distillate, from which the quality of the pitch remaining in the still may be foretold.

If the distillation is continued too long, much damage is done in several ways. In the first place, the anthracene is too much contaminated with chrysene and pyrene. Much of the pitch is turned into coke, sometimes to such an extent that the pitch ceases to run out of the still; and even if it does run, it will not solidify in a glass-like, but in a porous, honeycombed form, and is quite unsaleable. Lastly, the still itself is much damaged by this treatment.

It should, however, be noticed that the "coking," which is a very much dreaded trouble in the distillation of tar, is not merely a consequence of continuing the distillation too long, but it also depends upon the nature of the tar. It has been observed that tar obtained from pure coal (whether in the gas-retort or in the coke-oven) has a comparatively slight tendency to coking, but gas-tars, obtained from coal mixed with lignite, bituminous schists, and other substances of this kind, show this tendency more strongly, together with retaining water very tenaciously, and thus increasing the tendency to boil over.

E. Kopp[1] proposed driving off only a portion of the creosote oil and *distilling the soft pitch to hard pitch in a special still.* He asserted that he had found in such soft pitch from the Turin gas-works 4 to 6 per cent. anthracene; but this seems very improbable, and it should be remembered that at that time no exact methods for estimating anthracene were known. The pitch-still was to have a greater width than depth; the gas-pipe was to be of large bore, to join the still only 6 or 8 inches above the level of the boiling pitch, and then to bend down at once, in order to carry away more readily the heavy vapours. Towards the end the distillation was to be promoted by a current of superheated steam, or of heated air which had been passed through a red-hot pipe filled with charcoal, and thus converted into a mixture of carbon monoxide and nitrogen. During the distillation as much melted pitch as corresponded to

[1] Bolley-Kopp's *Spinnfasern*, p. 381.

the oil distilled was to be run into the still by means of a pipe reaching through the still-cover half-way down into the pitch; this would amount to half as much as the original charge of pitch in the still. The steam or heated gas was to issue either immediately above the surface of the boiling pitch or within the same. Lastly, when the contents of the still had become too thick they were to be expelled by the steam or air, the cooling-worm having first been shut off. We do not know whether Kopp's proposal has ever been carried out in practice. That part of it which refers to promoting the distillation by a current of steam or gas has been proposed and carried out elsewhere (see below). There remains the proposal to effect the distillation to hard pitch, not in the same still from beginning to end, but transferring the last stage to a separate vessel. This would not be very easy to do, and would not pay unless more anthracene was got out, which has not proved to be the case.

We must distinguish between this distillation of soft pitch up to the stage of hard pitch, and that of hard pitch itself to coke, which will be described in the next chapter.

Employment of Steam in the last Stage of the Process.

Apart from what would happen if hard pitch were run off too soon, the still-bottom naturally suffers considerably during the last stage of the process, when the heat has risen to a high point, especially where it is not protected by a curtain-arch. At the same time the vapours now formed, which are very heavy, cannot so easily get out of the still into the worm, the level of the mass being now very low, and the upper part of the still not being heated; a portion of these vapours must condense again within the still itself; and the distillation is but sluggish. The longer it lasts, the more opportunity there is for the hydrocarbons to split up into carbon and permanent gases. Hence it seems rational to promote the carrying-away of the vapours at this stage, either by superheated steam, etc., or by a vacuum, or both.

Steam appears to have been employed for a long time past to promote the distillation, not merely at the commencement, as described, pp. 312 *et seq.*, but again in the last stage, when it must, of course, be first superheated.

It is, for instance, mentioned in Cormack's patent, No. 1368, 2nd June 1864. According to Watson Smith, Mr John Barrow, in Manchester, employed steam as a secret process about the same date. I am informed by Mr S. B. Boulton that the introduction of steam is fully described by Dr Gesner in a work upon *Coal, Petroleum and other Distilled Oils*, published in London, Paris, and New York, 1865; also that Mr Boulton experimented with steam in 1865 and 1866, in conjunction with M. Audouin, and that he had used it for many years past. Steam is also mentioned in Audouin's patent of 1872 (see next page), but only as a means of stirring up the contents of the still. The use of steam, however, did not become general until recently. At the present time every well-appointed tar-works possesses tar-stills provided with steam; and by that means most of the troubles formerly caused by quickly destroyed bottoms, by explosions, etc., have vanished.

The steam fulfils several purposes. It assists in carrying away the vapours as before mentioned; this shortens the time required for the distillation and increases the yield: besides, it prevents the pipes from being choked up. Thirdly, the formation of hard crusts upon the still-bottom is lessened by the temperature being there kept comparatively low, and also by the agitation of all the contents of the still, so that coking and burning-on of the pitch cannot easily take place. Indeed, Trewby and Fenner assert that with their system, shown in Figs. 88 and 90 (pp. 332 and 334), no coke at all is formed on the still-bottoms, and thus cleaning out the still becomes unnecessary. At all events, the Beckton stills go for many months without cleaning. Elsewhere experience has not been quite so favourable, perhaps because the steam was introduced by a simple cross of tubes, etc.; whilst by Trewby and Fenner's plan steam ranges over every part of the still-bottom, issuing from numerous and suitably-formed outlets. For this reason we have adopted their system (introduced at the great Beckton works) in our diagrams, without undertaking any responsibility if it should be found too complicated and the outlets too liable to be choked up. Of course any similar arrangement will answer the same purpose. The arrangement described (but not figured) in Audouin's patent of 1872 already consisted in projecting jets (of carbonic acid, combustion-gases, steam, and

the like) in all directions, preferably downward, and near to the bottom and sides of the distilling-apparatus.

The pressure of steam employed in tar-stills usually ranges from three to five atmospheres.

A further question is: In what way is the steam to be superheated? At a German works the superheater is a coil of $\frac{3}{4}$-inch wrought-iron tubing, with a bottom surface of 3 ft. 3 ins. square, placed in an oven-like space above the fire-arch. The boiler-steam is first freed from liquid water in a suitable catchpot, and then enters the superheater, where it attains a temperature of 275° C. The steam-pipe, where it issues again, is covered with a thick non-conducting coating, and runs over the top of the still (which has the shape of a steam-boiler), into which it sends four branches. Each of these is provided with its own cock, and also with a special air-cock, through which the steam is blown off for a moment in order to remove any condensed water, before the cock leading into the still is opened. This arrangement has been in operation ever since 1873, and gives perfect satisfaction. The steam is first blown in when the change is made for anthracene oil—that is, when the thermometer has got up to 270°. From this time to the end of the process no more firing is required; the heat stored up in the arch that runs all along the still-bottom, together with the superheated steam, suffice to finish the distillation. After the anthracene oil has been got out, creosote oil is pumped into the still, to make soft pitch or "prepared tar" (*cf.* Chapter VI.), which lowers the temperature so far that the still can be emptied at once and recharged.

A similar system of completely dried and then superheated steam I found at another German works, employed with stills of the usual cylindrical form with concave bottom, and giving entire satisfaction.

Some English manufacturers do not superheat the steam at all, as they find that in their system, where it is conducted through the tar in so many fine jets, it is by this alone superheated to the temperature of the tar. But I have observed also at a German works, where the steam was simply introduced by a cross of tubes, that no special superheating took place, the superheater formerly employed having been dispensed with. But the steam was previously dried, and caution was always

used in first starting it, as any water carried into the still would cause an explosion when suddenly brought into contact with tar standing at a temperature of 300° or more. This has actually taken place at several works. For that reason alone we would advise in any case such a slight previous superheating as will *completely* dry the steam, which can be done without any expense whatever.

The employment of dry steam at the end of the process has the further advantage that in running off the pitch no air need be admitted into the still, which otherwise might lead to explosions or fire.

Cabot (Amer. P. 184182) seeks to promote the distillation of anthracene by blowing *petroleum* into the mass—a process of very doubtful value.

Mechanical Agitators in Tar-stills.

Sometimes mechanical agitators are employed in tar-stills in order to avoid superheating the bottom at the end of the process. Thus Berninghaus (Ger. P. 4586) provides the still with a stirring-apparatus like a ship's screw. Lennard (*J. Soc. Chem. Ind.*, 1883, 239) employs a horizontal cylinder, 20 ft. by 7 ft. 6 ins., provided with an agitator. Fenner (B. P. 13629, 1884) combines mechanical agitation with the action of steam, as described p. 339. Mechanical agitators are also mentioned in Audouin's patent (No. 1456, of 1872), along with agitation by means of a stream of illuminating-gas, carbon dioxide, air, smoke-gases, or steam. It is asserted that in this way 10 to 15 per cent. more anthracene is obtained than usual.

Mechanical agitators are especially found useful when distilling tar very rich in fixed carbon, which sometimes occurs in large quantities, and in distilling the tar causes the formation of hard crusts of coke at the bottom of the still. This is prevented either by injecting superheated steam, as before mentioned, or by a mechanical agitator, consisting of a revolving shaft with chains dragging along the bottom. In one trial with this apparatus, after fifteen distillations the still-bottom was found to be almost quite clean, and much less coal had been used for firing. The rivet-heads, as well as the links of the chain, were certainly ground off, and it was found necessary to renew the chain and to re-rivet the still-bottom after six months,

but this last drawback could be avoided by countersinking the rivets. There was no deformation of the still-bottom. In this way it became possible to distil such tar down to hard pitch, which was softened again by the addition of dead oil.[1]

It does not seem necessary to employ agitators in the case

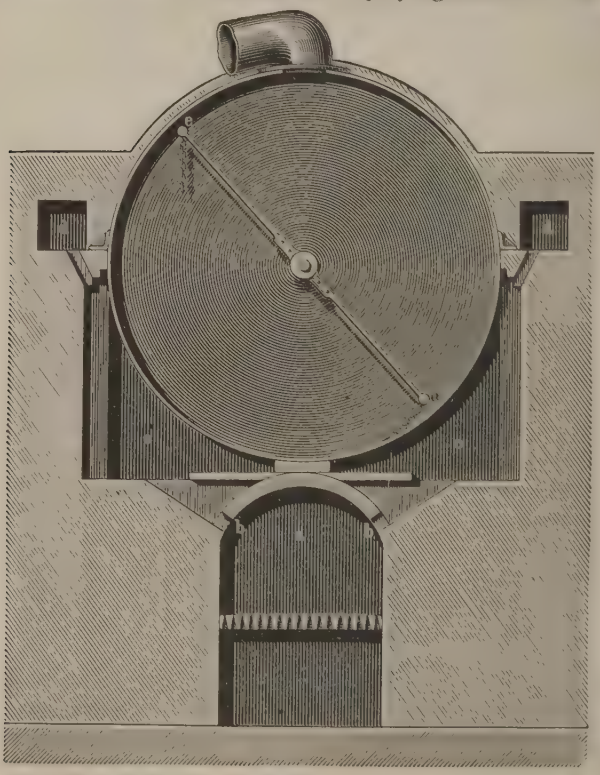


FIG. 106.

of ordinary tars. At Beckton, where Fenner's agitators had been introduced in some of the stills, Mr Wilton found no advantage against the system of simply blowing in steam during the latter part of the distillation, and the use of the agitators was therefore discontinued.

[1] *Wagner-Fischer's Jahresber.* for 1885, p. 464.

At some Scotch works mechanical agitation is employed, not during the distillation itself, but at the end, when heavy oil is run in for the purpose of softening the pitch. This is done at Dalmarnock, Glasgow (Messrs George Millar & Co.). Figs. 106 and 107 show the stills there used, as described in Dr Ballard's *Report to the Local Government Board for* 1878 *and* 1879, p. 139. Several stills, in the shape of horizontal iron cylinders, 21 ft. long and 8 ft. 6 ins. diameter, are placed side by side in a set. The heat from the fire *a* does not impinge directly upon the bottom of the still, the fireplace being arched over along its whole length (*cf.* p. 324). The fire-gases pass through twenty openings (*b b*), on each side of the arch into the flue *c c*, and thence through similar openings into the flue *d d*, leading to the chimney. The still-bottom touches the arch, but does not rest upon it, the still being suspended by stout

FIG. 107.

angle-irons from the side masonry. In order to keep the inside of the still-bottom clean, horizontal bars (*e e*), shown in elevation in Fig. 107, reaching to within 3 ins. of the shell of the cylinder, are made to revolve. To these bars are attached, at intervals of a few inches, short pieces of iron chain which drag along the bottom and prevent deposition. The chains are arranged upon the bars so that those of the one bar scrape the cylinder-bottom in the places in which it is not scraped by those of the other bar. This apparatus lasts for many years without repairs.

Fig. 108 shows the arrangement of stirring-apparatus for an upright still, holding $7\frac{1}{2}$ tons, and worked with a vacuum. The advantage of all such apparatus is doubtful, and they are only exceptionally employed.

Distillation in a Current of Inert Gases.

Craig (B. P. 7615, 1907) distils blast-furnace tar with *an inert gas*, such as blast-furnace gas, producer gas, or flue gas, instead

of air, in order to prevent oxidation, and to improve the quality of the pitch and oil produced.

Employment of a Vacuum in the Still.

The diminution of pressure within the still by means of a

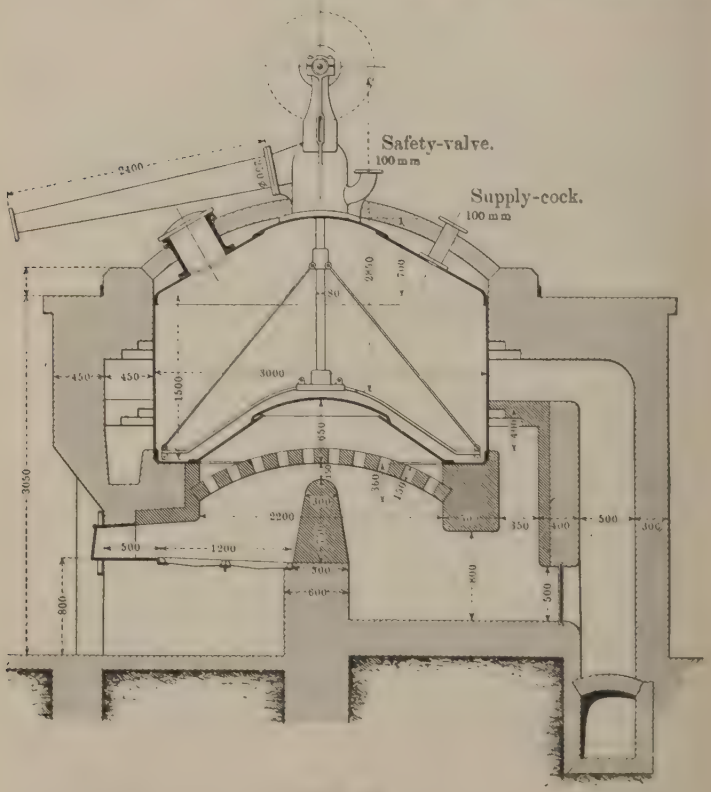


FIG. 108.

vacuum-pump has very great advantages and is more and more coming into use. The author saw it first performed (in 1880) at a German works in the following manner. The distillation is commenced at the ordinary pressure, and continued till it is time to change for anthracene oil. Now a steam-pump is

started, which aspirates both gases and oils away from the condensing-worm into a large boiler sunk in the ground, where the anthracene oil remains whilst the gas is forced out by the pump. From the same pipe steam is injected into the still, as above described, but merely to keep its bottom clear; for no choking-up ever happens, even without the steam: the pump sucks away the butter-like mass quite easily into the boiler. The vacuum-gauge in this showed 15 mm. mercurial pressure. On their passage through this boiler the products were cooled, so that the gas coming out of the far end entered the pump nearly cold. When the distillation was finished, the same boiler served as a pressure-apparatus for forcing the oils into the anthracene-crystallizers. The whole arrangement answered

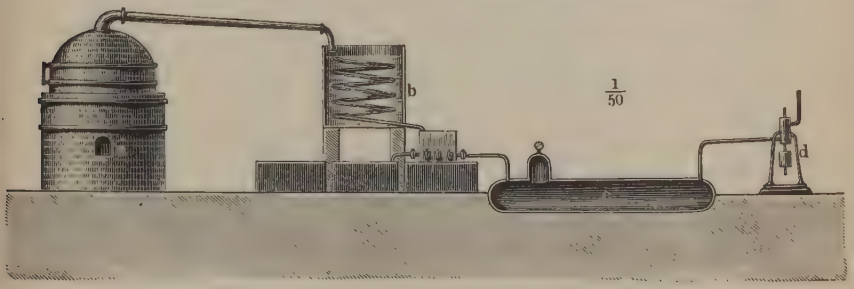


FIG. 109.

so well that a second apparatus of the same kind had been mounted for creosote oil; but this had not started at the time of the author's visit. The greatest advantage of this plan is the regularity of working, and the complete absence of any danger of choking-up the pipe. An injector had been tried in lieu of the steam-pump, but had not answered so well. The sketch (Fig. 109) may serve for elucidating the process. In this, *a* is the tar-still, *b* the condensing-worm, *c* the anthracene-oil-boiler with its dome, vacuum-gauge, steam-pipe, etc.; *d* the air-pump.

The pressure within the still in this way is usually brought down to about 4 ins. of mercury, and the boiling-points are thereby lowered about 80° C., which not merely hastens the process, but is of decided advantage for the quality of some of the products, especially the anthracene.

The first introduction of the vacuum in tar-distilling appears

to be due to Mr S. B. Boulton, who applied it in more widely extended ways than that just described, and in such a manner as to prevent all nuisance. The following description of his arrangement is taken from Dr Ballard's Report to the Local Government Board for 1878 and 1879, p. 142:—"But the most perfect arrangements for preventing nuisance from uncondensed and non-condensable vapours and gases that I have seen are at Messrs Burt, Boulton, and Haywood's works at Silvertown, near the Victoria Docks. From each condenser the condensed and uncondensed matters pass into a receiver having an opening at the top, which is firmly closed down, during working, with an accurately-faced iron cover. Out of this receiver the condensed liquids are drawn off below to the store-tanks, while the uncondensed gases and vapours are drawn off above by an air-pump or gas-exhauster, worked by a small steam-engine provided for the purpose. These gases and vapours from all the whole row of receivers pass into an exhaust-main, which communicates with two 'washers'—the first arranged like a chemist's Woulffe's bottle. They have to pass through both of these, where a certain amount of further condensation takes place. They then pass through the exhauster to a third condenser or 'washer,' shaped like a boiler; and here again they have to pass through water and over water for some feet to the discharge-pipe, which conducts such as are still uncondensed to a fire, where they are consumed. This exhausting arrangement has the further value of assisting to draw off the products of distillation from the still, and to clear this of offensive gases which would otherwise escape into the air during the process of recharging with tar. Another advantage which these manufacturers say they thus obtain is that the watery vapours (containing sulphide of ammonium) which accompany the naphtha and benzol series of products, and which were formerly wasted, are now collected and utilized for the manufacture of sulphate of ammonia. The benzols also themselves are increased in bulk from the greater care with which these lighter vapours can be collected. Further, by the use of the air-pump and the closed receiver, the duration of the whole distilling operation is abridged very sensibly, which is itself a source of great economy in a large manufactory."

A somewhat complicated apparatus for distillation (of

alcoholic liquors) in a vacuum has been constructed by N. Galland (Ger. P. 17972, 1881).

Krey has so greatly improved the apparatus that the fractions can be changed without interrupting the vacuum, as shown in Fig. 110. The end of the worm *a* is connected with the cast-iron "pear" *b*, shown here without its cover. The cover is ground on, and is provided with "sights" made of hardened glass. The three-way cock *c* communicates through *f* and *f'*

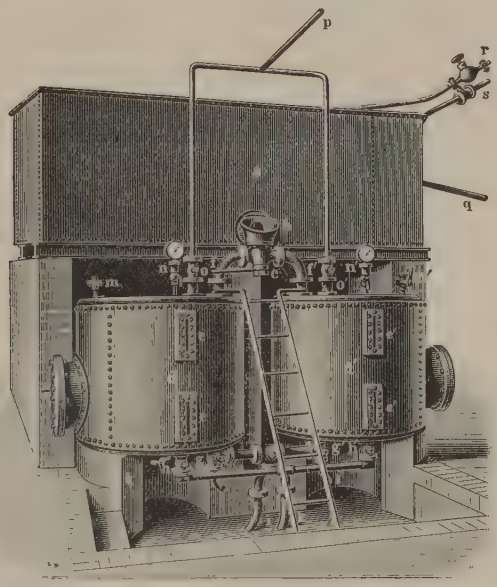


FIG. 110.

with the receivers *d* and *d'*. These are provided with glass "sights" (*e* and *e'*), pressed against the faced edges with asbestos packing on one side, and two indiarubber washers on the other. They are further provided with vacuum-gauges (*n n'*), air-cocks (*m m'*), blowoff-cocks (*g g'*, *h h'*), and manholes; with the air-pump they are connected by the cocks *o o'*, and the branch-pipe *p*. We also notice the steam-pipe *r*, water-pipe *s*, and overflow-pipe *q* in the cooler.

During the time the first runnings and light oil are distilling

the "pear" *b* is covered by an ordinary glass jar. As soon as the creosote-oil period begins the air-pump is started, the receiver is changed, and the pear is closed with its cast-iron cover. The vacuum acts only upon the receiver actually at work, and is cut off from the other receiver by the three-way cock. The previously filled receiver is emptied through one of the cocks *m m'* or *g g'* by the pipe *i''*, into a store-tank below, the ammoniacal liquor having been first run off through *l* or *l'*. If the receiver at work is filled, or if the state of the liquid as observed through the "sights" calls for changing the fractions, the empty receiver is connected with the vacuum-pump, and when this has operated sufficiently the three-way cock *c* is quickly turned round. The oil contained in the full receiver, when the vacuum-cock has been shut and the air-inlet opened, is run out by *h h'* and *i'* into a pressure vessel below, and forced from this into a collecting-tank. Thus the work is continued until the still is finished.

I am informed by Dr Kraemer that he introduced that system already in 1881 in all the factories belonging to the Aktien-Gesellschaft für Teer- und Erdöl-Destillation, and that they merely applied it to the treatment of browncoal-tar.

Although there is no difficulty in taking samples for testing the distillates during the vacuum distillation, some prefer to work off a still without the vacuum; thereby the bulb of each fraction is fixed, and this serves later on as guidance for the vacuum distillation. During the last period the firing is discontinued, and when all the oil desired has distilled over the vacuum-pump is turned off and the air is slowly admitted into the still through the receiver.

The quality of the distillates is decidedly improved by the vacuum distillation, and the yield, especially of anthracene, is increased. The objections opposed to this plan by Kissel (*Z. angew. Chem.*, 1893, p. 61) are certainly unfounded, especially as most tar-works do *not* employ mechanical agitators for vacuum stills (as he believes to be the case). On the other hand, the principal works employ steam and vacuum combined, as described above.

Weyl (Ger. P. 153222; B. P. 12122, 1904) describes an apparatus, intended for a very high vacuum, consisting of a kind of locomotive boiler, a horizontal cylinder with a fireplace

in front and many heating-tubes inside, completely surrounded by the tar.

Running off the Pitch.

When working in the old manner (*i.e.*, without steam, etc.) it is necessary to fire up to the end, and that sharply. As soon as it is considered that the operation is at an end, the fire-door is opened, the coals are drawn out, and soon the distillation ceases. But the pitch cannot be run off at once, partly because there is danger of its taking fire, and partly because the large amount of heat stored up in the still and the brickwork might damage the still. There are also very acrid vapours given off by the hot pitch which are objectionable to the neighbours, although they do not seem to be actually injurious to health, and it is even a fact that children suffering from skin and lung diseases, are brought to tar-works to inhale those vapours, frequently with a curative effect. Hence some time must elapse before the pitch can be run off with the precautions prescribed above—two, six, or even twelve hours, or even longer, according to the size of the still. After the pitch has been let out, some hours must again elapse before coal-tar is pumped into the hot still, lest the sudden contraction on cooling should start the rivets, etc. At first sight it would seem most suitable to wait rather longer before letting out the pitch, and thus further to diminish the danger of its taking fire ; but it is much more important that the pitch should be perfectly liquid when run off, so as to leave the still completely empty. The outlet-cock must be arranged with the same view. Whatever pitch remains in the still is changed by the heat retained by the brickwork into coke, which covers the still-bottom as a non-conducting layer, does not dissolve in the fresh tar, and would soon cause the bottom to be burnt away if it were not from time to time knocked off and cleaned out like boiler-scales. In the case of ordinary English stills this must be done after three or four distillations ; but proper placing of the cock, protecting the bottom by a curtain-arch, and twelve hours' rest, will prolong the time to about a month.

The treatment of the stills, as regards running off the pitch, is very much facilitated by the use of steam during the last process, and this is not one of the least reasons for introducing the steam treatment. But the operation is very much simpler if *the pitch is softened in the retort* before running off. In this

case the distillation is, in the first instance, carried on so far that the residue, if it were run out and allowed to solidify, would yield "hard pitch." This is, however, not done, but creosote oil or the oils draining from anthracene (see Chapter VII.) are pumped back into the still containing the liquid pitch, and thus mixtures are produced of any degree of viscidity, or even liquid at the ordinary temperature, the latter being sold as "prepared tar" or "refined tar." The mixture of the liquid pitch and the oils pumped into it takes place without any special appliance, but it is, of course, promoted by mechanical agitation, for which purpose the Scotch stills, shown in Figs. 106 and 107 (pp. 376 and 377), have been especially constructed.

Where the pitch is softened in the stills themselves no choking-up of the outlet-cock or taking fire of the pitch in the air on running off need be feared; and crusts of coke on the still-bottom would probably not appear to any great extent, even if steam were not applied, as is now almost universally done.

An outlet-cock can be dispensed with altogether if the soft pitch, after some cooling, is forced out by means of perfectly dry steam or of a vacuum through an upright pipe that comes out of the still-top and conveys the pitch to some safe place. The outlet-pipe should start from the bottom of the still (which in this case may even be convex), and rise perpendicularly to the highest point, and thence descend in a gentle curve; it must be heated up by steam before the forcing begins. There is in this case no danger of any fire in the pitch-cooler; and the process has answered quite well at several works (*cf.* the sketch, Fig. 94, p. 341). But this plan is suitable only for very soft pitch, and in the cold season it gives so much trouble that it cannot be recommended.

At some Scotch works the soft pitch is pumped out from the top of the still, without any exposure to the air, through a close iron conduit, to the pug-mill, in which it has to be manufactured into "asphalt." If this conduit be sufficiently inclined, no cleansing of it will ever be required.

Running off the *soft* pitch (which is not so very hot, and does not take fire in the air nor choke up the cock) is thus easy enough. But the case is different when *hard* pitch is to be run off. Here not merely must the pitch be allowed to cool down

to some extent within the still, but it must first be run into a receptacle protected from the air, in which it must remain till it gives off no more vapour and is no longer liable to take fire in contact with the air. Then it is let off into the open pitch-holes to solidify. In this case the outlet-cock of the tar-still should be provided with a cleaning-flange, and with some contrivance for heating it in order to melt the adhering pitch. This is best done at the end of each operation, before the still is charged again; it is then attended with much less danger than is incurred by deferring the heating till it is time to run off. For this purpose the plan shown in our diagram (Fig. 113, p. 390) can be recommended. The cock is placed in a recess of the still-wall; and at each side of it, separated from it by thin walls, the flues descend: if this should not keep it warm enough, a small fire of wood-shavings can be made round it in the recess; or this is filled with sand, which is heated by a small fire. Sometimes a steam-coil is wound round the cock; but steam-heat is frequently not sufficient for melting hard pitch. In any case the cock must be situated at the opposite side to the fire-door, lest the vapours given off from the running pitch be set on fire.

The outlet-cock is connected by a short descending pipe with an iron or brick spout covered over with an iron plate, for conveying the pitch into a chamber where it is to undergo its first cooling (the pitch-cooler). A spout is preferable to a pipe unless the pitch-cooler is immediately beside the still, because the pitch readily solidifies in this part of its course, which does less harm when it takes place in a spout than in a pipe. The cover of the spout is spread over with earth to keep off the air and prevent cooling; but, notwithstanding, there is always a coat of solidified pitch in it, which must be hacked out afterwards. If the air is not excluded here, the pitch may easily take fire; and the flame would travel to the pitch-cooler, in which case an explosion would be almost certain to follow. The spout must have sufficient fall and no sharp curves. On account of the danger of fire, some prefer a closed conduit from the still to the pitch-cooler, but they will have much trouble by its choking-up.

In the *pitch-cooler*, *pitch-oven*, or *pitch-house* the pitch must be left long enough (say five or six, or even twelve hours) to

cease giving off vapours and to run no risk of taking fire when brought into the open air. This cannot be done without the pitch getting rather tough; hence a good deal of it remains behind in the pitch-cooler, and must be hacked out from time to time. The pitch-cooler is either a brick chamber with brick floor and arched top, or else any sort of iron vessel, for instance an old steam-boiler. A brick pitch-house for two 20-ton stills is about 20 ft. long, 7 ft. wide, and 8 ft. high to the crown of the arch; some are very much larger. Each gable-end is provided with a 3-ft.-square manhole, closed by iron doors luted with clay. At one gable-end the pitch-spout enters; and at the opposite end there is a tap-hole just above the bottom, plugged with clay or with an iron bar, from which open spouts lead to the different pitch-holes.

Iron pitch-chambers are either cylindrical or square; they are more expensive, and suffer more by the hacking out, but cool much quicker than brick chambers. The latter have no sensible advantage, since even in a brick chamber the pitch is cooled long before the chamber is needed for the next charge. Iron coolers, indeed, often act too quickly, and cause the pitch to solidify too early, so that they have been sometimes provided with a fireplace, which, however, may cause coking of the pitch. Where the pitch is softened in the pitch-cooler by adding creosote oil, there is, of course, hardly any trouble with solidifying.

The longer the pitch is left in the cooler, the less nuisance is produced; its temperature, on running out, ought not to exceed about 120°, and very little vapour is then given off. There is also this additional advantage, that the oily vapours, which cause the nuisance, are thus reabsorbed in the pitch, and make it softer, which means more valuable. But the longer the pitch remains in the cooler, the stiffer it becomes; if kept too long, the discharge-pipe gets choked, in which case the workman generally clears it with a red-hot iron. This proceeding occasionally gives rise to an explosion, and can be entirely avoided by enclosing the discharge-pipe in a steam-jacket.

The pitch-cooler must have a vent in the roof for the escape of gas. This is mostly open to the atmosphere; but it is best to carry it to the chimney-shaft in a slanting tube, so that any condensing liquid may run back; or to make it dip about an

inch into a vessel filled with water, similarly to the plan adopted in Paris (see below).

A tap adapted to viscid substances, such as partially cooled pitch, is shown in Fig. 111.

F. Lennard (B. P. 4547, 1883) places within the (iron) pitch-cooler a number of wrought-iron pipes, through which cold tar is pumped so as to cool down the pitch and to obtain a preliminary heating; or else he effects the same object by different arrangements of the pitch-cooler.

FIG. 111.

Petersen-Kinberg recommends for tar-distilleries manufacturing roofing-felt a pitch-cooler which at the same time serves as montejus. It is boiler-shaped, 5 ft. diameter 15 ft. long, placed in a somewhat slanting position, with an inlet pipe for compressed air, a pipe in the top, provided with the following fittings: a tap, for letting out the air during the filling; an ascending pipe, reaching nearly down to the bottom, for forcing the liquid pitch into the receiver for "prepared tar" (there must be a contrivance for cleaning this pipe when the contents of the boiler have turned too stiff); and a running-off valve, which the inventor, after working it with full success for a number of years, protected by a German patent. This is shown in Fig. 112. A very slight force, exerted upon the hand-wheel *a* is

FIG. 112.

multiplied many times by means of the screw *b* and the toothed wheel *c*, so that the valve *d* is forced down upon its seat with sufficient intensity to resist any desired pressure. (This contrivance is sold by C. F. Scheer & Co., Feuerbach, near Stuttgart.)

Sometimes no pitch-coolers are provided; the pitch is then left to cool in the still itself till it can be run straight into the open pitch-holes. This plan is decidedly not advisable for *hard*

pitch; the stills must be allowed to rest much longer, and they must be cleaned out by manual labour after each operation.

Lastly, the *pitch-holes* or *pitch-bays* are situate in front of the pitch-house, and connected with it by brick or stone channels, having a good incline and provided with movable covers. They must have a perfectly level brick floor and 18-inch side-walls; but otherwise their shape is quite indifferent and may be adapted to local circumstances. They should be of sufficient area to make it unnecessary for the pitch ever to fill them to a greater depth than 12 ins.; preferably only 8 ins. There must be at least two pitch-holes, to serve in turn, so that at all times the pitch may completely cool down and solidify in one of them. In the heat of summer this is sometimes promoted by squirting water over them. It is expedient to whitewash the floor every time before using it again, to make it perfectly smooth and to facilitate detaching the pitch. Some, for the same purpose, use ordinary street dust for this purpose, but this always causes a slight deterioration of the quality. Hard pitch becomes so brittle that it is easily hacked up with a pick in large lumps. The dust unavoidably formed is most irritating to the mucous membranes of the eyes; the men ought therefore to protect their eyes by "goggles" or by crape; and this kind of work is always done by preference at night. In summer it is of course more disagreeable than in winter.

Watson Smith points out that the pitch-holes ought to be laid out so that no pools of rain-water can remain in them: otherwise the pitch may become honeycombed and much less saleable.

At some works the bays are entirely covered over with boards, or are enclosed in a galvanized iron chamber, provided with movable shutters, to avoid any nuisance.

At the smallest tar-works there are sometimes no pitch-bays, but the pitch is ladled or pumped out of the cooler into tubs, casks, etc. In this case explosions occur sometimes in running in pitch from the stills, just after a pitch-house has been cleaned from the solidified pitch by hacking it up (Hirsch, *Chem. Zeit.*, 1884, p. 136), evidently because after that operation the pitch-house is filled with fresh air, which sets the pitch-vapours on fire as the contents of the still are running off.

According to Dr Kraemer (priv. comm.), the fires in pitch-

houses are generally caused by the fact that the hot pitch chars the wooden parts of the roofs and sets them on fire. He has never observed any explosions. Some ascribe the explosions occurring in pitch-coolers to the fine particles of carbon and pitch floating about in the air; but no doubt these alone would hardly be dangerous without the vapours equally filling the space. Blowing-out the cooler by dry steam after each operation would probably remove all danger from explosions.

Instead of the apparatus just described, a more complete arrangement has been made at the Paris gas-works—an arrangement proposed by Regnault, and which is also found at a large English tar-works. It is represented in Fig. 113. The pitch leaves the still by the cock *a* and a pipe *b* (provided with a cleaning-neck) and runs into the iron box *c*, in which it remains a few hours, till it has cooled down to 200°. From this it goes through the cock *d* and the pipe *e* into a wrought-iron chamber (*f*) half sunk in the ground, 7 ft. wide, 30 ft. long, and 10 ft. deep, which receives the pitch of a number of stills. Along its whole length runs a brick pit (*h*) 5 ft. deep, communicating with *f* by holes (*g*) near the bottom. An iron plate (*i*) prevents the pitch as it comes from *f*, at a temperature of about 120°, from rising at once to the surface; it can only pass along the edge of *i*. The pitch in *f* and *h* remains liquid from one operation to the next, being protected from quick cooling by the ground. But on the surface of the pitch above *i* a hard, elastic crust forms; this is promoted, if necessary, by running water over it. Now, if fresh, hot pitch runs out of *a*, it flows in *f* on to the surface of the partly cooled, but still liquid pitch from the last operation; it forces this through *g* into *h*, the still colder contents of which rise past *i* and flow away underneath the crust at *k* into the open pits *l*, where they are left eight or ten days for entire solidification. The very hot pitch in *f* has in the interval time to cool down; the vapours rising from it and in *c*, which communicate by the pipe *m*, are condensed by the surface of iron in contact with the air, and are reabsorbed by the liquid pitch. The pipe *n*, which dips into a vessel filled with tar, allows the air to escape as the tar runs in, and also serves as a kind of safety-valve. But, besides, *f* is provided with a loose manhole-lid, merely luted by Scott's cement, etc., which

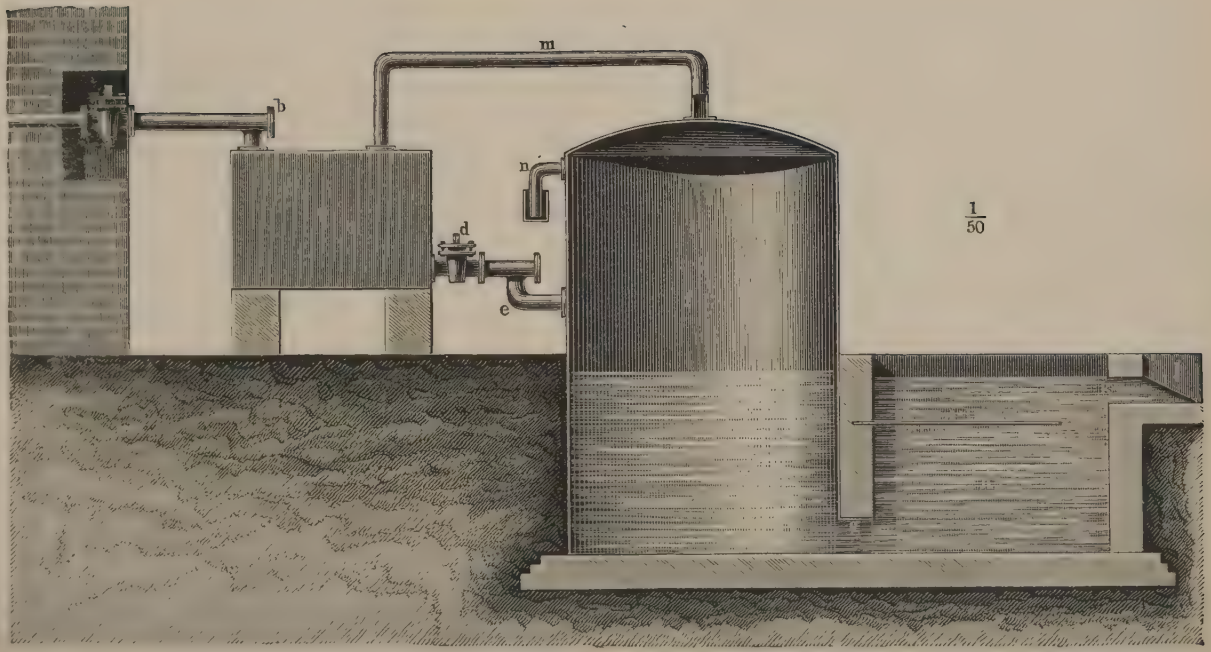


FIG. 113.

likewise performs the office of a safety-valve. This apparatus completely does away with all danger of fire, and with the nuisance arising from the heavy yellow or white, extremely irritating vapour given off by the hot pitch, which will travel as a compact cloud near the surface of the ground to great distances. Whilst observing that pitch was being run off, by the flowing away of tough pitch from the hole *k*, I could not perceive the slightest smell, although standing close by.

These vapours are extremely disagreeable to most persons; but the Government Inspector, Dr Ballard, reports that the only bad effect upon health that he heard of was that they sometimes produce headache, giddiness, faintness, nausea, and perhaps some oppression of the breathing, but never any very serious or permanent ill effects (cf. *supra*, p. 380).

The above apparatus can be introduced only at very large works where pitch is run off several times a day; otherwise the old charge would stiffen too much before a new charge is run in.

According to Dr Kraemer (priv. comm.), the tap (shown in Fig. 113 at *d*) is preferably placed in a box, divided into two chambers by a diaphragm reading not quite to the bottom. The hot pitch runs into the first chamber and forces the partially cooled pitch below the diaphragm into the second chambers, from which it gets into the pitch-cooler. (This is practically done in our figure by the pieces *f*, *g*, *h*, *i*, and *k*.)

At smaller works (distilling not above 10,000 tons tar per annum) it is advisable, in lieu of a pitch-bay, to run the pitch into moulds which can be taken to pieces and thus furnish the pitch in loose blocks, without hacking it out. Such moulds can be made cheaply by cutting old tar-barrels or petroleum-barrels in two, which gives two tubs, from which the pitch can be removed by loosening the hoops and staves. More durable are iron moulds of similar form. They are best placed on a platform, fixed or revolving, and filled from a shoot provided with plugs at suitable distances. Tubs made from old petroleum-barrels (two from each barrel) hold $1\frac{1}{2}$ cwt. of pitch or a little more; a 15-ton still requires 12 rows of 10 tubs each. When containing moisture, they cause the pitch to froth up when run in for the first time, but never afterwards. They need not be painted inside with lime-water or the like; after turning over and loosening the top hoops, the block of pitch

comes away by a slight tap with a hammer. To run off the pitch from a 15-ton still occupies two men two hours, and the knocking-out from the tubs takes but little longer. The pitch is at once ready for putting into trucks, without any troublesome hacking out, and is quite clean. Both hard and soft pitch can be treated in this way, but in the hot season the knocking-out must be done in the early-morning hours. The worn-out tubs are used for firing-up, which is just the fate the old barrels would have suffered in any case.

Iron moulds are made in two pieces, connected by hinges, with a loose bottom. These must be painted inside with lime-water, or a suspension of clay in water, or, best of all, with cheap paraffin oil or some other oil which does not dissolve pitch.

A table in the Alkali Report, No. 30 (1893), pp. 22-29, gives the following data for all English tar-works:—Number of stills, size of the same (from 2 to 40 tons, mostly 10 to 12 tons), description of pitch-cooler, in a few cases the temperature at which the pitch is run off from the still into the cooler (between 100° and 280° C.) and from the cooler into the open bays (between almost the ordinary temperature [?] and 243° C), and the means employed for removing the noxious vapours and those for producing the necessary draught.

Continuous Distillation of Tar.

Frequent attempts have been made to render the distillation of tar a continuous operation, involving a constant inflow of fresh tar and outflow of pitch. Mallet[1] causes the tar to circulate on a sufficiently long lead bath, where it successively gives off light and heavy oils, and at the end runs off as pitch. The fractionating is effected by making the tar pass round divisions which do not impede its circulation, but separate the vapours into two or three classes. According to Knab, nothing is gained by this plan.

A proposal made by Vohl[2] is likewise intended to carry out a fractional distillation at a constant level, especially in order to meet the disadvantage of the light oils being kept

[1] Gerard and Delaire, *Dérivés*, p. 11.
[2] *Dingl. polyt. J.*, clxxvii., p. 133.

back by the heavy oils. This is effected by the apparatus delineated in Fig. 114. A and B are cast-iron stills; C, a feed-pipe dipping 3 or 4 inches into the liquid; D D, manhole-lids; E, pipe for conveying the vapours given off in A to B; F, pipe for the vapours going from B to the separator G; H, pipe for the heavy oils, connected with a refrigerator; I, pipe for the light oils, also connected with a worm; K, connecting-pipe between the two boilers, with the stopcock U, to be opened and shut by the handle L, in order to let the

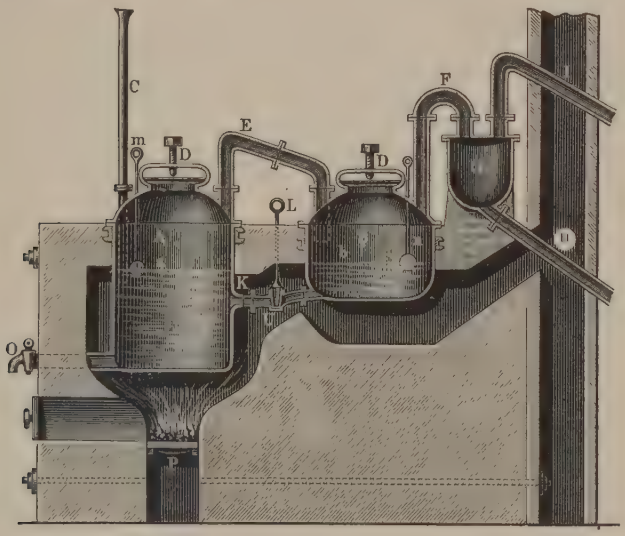


FIG. 114.

liquid flow from B into A. *m* and *n* are floats; *m* is so arranged that, on the liquid in A rising above the level *a*, the float shuts the supply-cock of C; *n* is connected with a loose valve which opens whenever the level rises too high. O, outlet-cock for the heavy oil residue in A; P, fireplace; V, stoking-hole. To start the apparatus, A is filled through C up to the level *a*, its contents heated to boiling, and then a continuous supply run in through C. Until the ebullition in A is very strong, the flame is kept off B by a damper, and is directed straight to the chimney.

Meanwhile B and G are getting heated, and from H a constant stream of oil distils off. Now by opening the damper the fire from P is directed underneath B; and from this time light oils distil from I, heavy oils from H; the heaviest oils remain behind in B. If *m* shuts off the supply-cock, the fire must be increased. Also, if the valve *n* in B is lifted, this is a sign of too little firing, too much being condensed in B; or else the damper keeping off the fire from B has been raised too late. When A has been worked off, which is soon known by experience, the fire is damped by wet ashes and the residue from A let off through a refrigerator (consisting of a set of cast-iron pipes immersed in water) into a tightly covered iron vessel. Then the contents of B are run through U and K into A, the level is made up to *a* by supplying tar through C, the damper for B is let down, and the operation is recommenced. Such an apparatus (erected by Thiriart & Co., of Cologne) is said to yield 1½ ton of light oils in 12 hours. It was originally intended for paraffin oils; but Vohl believed that it is also eminently suitable for coal-tar, and would yield twice the usual quantity of benzene and its homologues. It has, however, never been introduced for coal-tar and is not at work even for tar from lignite.

N. M. Henderson (B. P. 540, 1883) has constructed a similar apparatus, consisting of three horizontal cylinders, about 7 ft. diameter and 9 ft. long.

We pass over the patents of Ellison and Davis (B. P. 13929, of 1886) and of Max Böhm & Co. (Ger. P. No. 60747), to give a description of Lennard's continuous still (B. P. No. 7334, 1888), shown in Figs. 115 and 116. The still (C), divided into compartments (*c c*), partially dips into the oil-bath B. The compartments are arranged in steps, with inclined bottoms and with inlets and outlets at opposite sides, to force the tar to travel by the longest possible route. D is a steam-pipe, with branches (*d*) for each compartment, ending in perforated pipes. The compartments nearest to the tar-inlet pipe A have recesses (E) in their bottoms, with partitions (*e*). On one side of these the steam-pipe *d* and its dividing-pipes (*b*) are introduced. The tar enters at A, fills the recesses E, passes on the opposite side into the second compartment, and so on, being gradually distilled by the heat of the oil-bath and the steam until it has

been converted into pitch, which runs out continuously at F. The tar, before entering the still, is heated up to the boiling-point by a spiral (Y), lying in an oil-both (B), afterwards in a scrubber by steam passed through the opposite way. The vapours produced are condensed in some apparatus, cooled either by tar itself or by products distilled from it, which by this operation are redistilled and thus rectified.

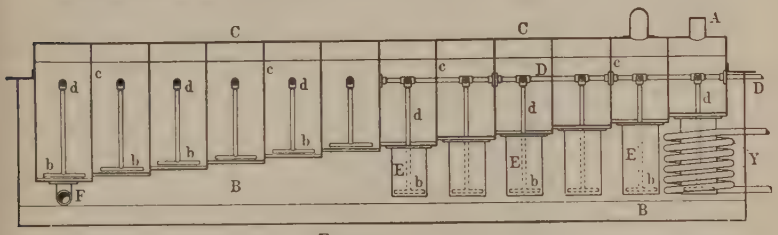


FIG. 115.

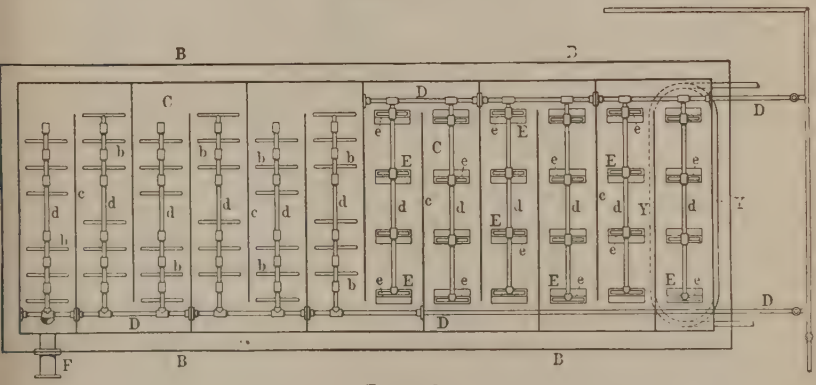


FIG. 116.

According to a later patent of Lennard's (No. 844, 1891), the tar, previously heated by being used as a cooling-agent, is superheated in closed coils of pipes, and on entering into a scrubber is freed from volatile matters by a current of steam, the pitch flowing away into a cooling-chamber and at last into pitch-bays. The superheating is done in sand-baths, fitted with iron worms.

The *Alkali Report* for 1894, p. 126, states that no noxious vapours are given out by this apparatus, but on the economical

success of the plan no certain opinion could be given. In 1895 there were two such stills at work at Messrs Forbes, Abbott, & Lennard's, at East Greenwich, one for 16,000, the other for 24,000 gall. of tar in twenty-four hours; also one in Scotland and another on the Continent.

During recent years this system seems to have come more into use. Löw-Beer[1] report very favourably on the Lennard stills in their present shape (Fig. 117). The raw tar, after being freed from coarser impurities by a sieve, is pumped by pump B, and is first employed as a cooling liquid in the creosote-oil

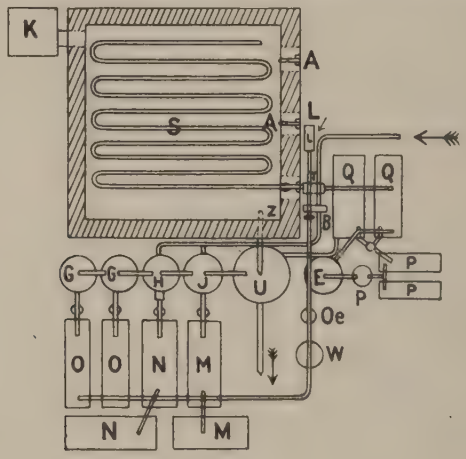


FIG. 117.

condenser H and in the anthracene-oil condenser J, and during this function it is already deprived of the ammonia water and of the lightest oils. It then passes through a "tar-scrubber" (E), consisting of a column filled with fireclay rings, and provided with an arrangement for heating it by means of superheated steam (which is merely used in the commencement, before the raw tar has had an opportunity of taking up heat in the oil-condensers, as described above). In the scrubber E the removal of the water and the lightest oils goes on, and is continued in a condenser (F), before the tar gets to the reservoirs, P P and Q Q. From these, still in a warm state, the tar is forced by a

[1] *Z. angew. Chem.*, 1905, 8.

pump (T) into the distilling-apparatus S. This consists of two cast-iron coils, one above the other, placed in a heating-furnace. The fall in these coils is quite regular, and amounts to 18 ins. in all. The diameter of this pipe increases towards the hotter, lower part, corresponding to the expansion of the tar by the heat, the difference of diameter between the beginning and the end of the coil being 2 ins. On leaving this distilling-coil at *z*, the tar has a temperature of 300°. It now runs into the "pitch-scrubber" U, where it flows over large surfaces, and is heated by a current of superheated steam to about 300°; here it yields the remainder of the volatile substances and leaves the scrubber in the shape of hard pitch, or, if desired, of intermediate qualities, as regulated by the temperature of the steam.

The vapours driven out by the steam get into a condenser (H), where the anthracene oil liquefies, and collect in N; they then pass the creosote-oil condenser J and the reservoir M, both of which, as before mentioned, are cooled by raw tar; this cooling can be regulated with such ease that the specific gravity of the condensed products does not vary during a number of months. The light oils leaving the condenser H are condensed further on by ordinary water-cooled coils in G G and collected in tanks O O.

The whole system, including the tanks for collecting the various distillates, stands under a vacuum of about 550 mm. (say 21 ins.). To prevent losses of ammonia and light oils, a water-tower (W) and an oil-tower (Oe) are placed between the tanks and the vacuum-pump L. There are also samplers, consisting of automatic siphons which act without destroying the vacuum.

The heating of the distilling-coil cannot be done by coal, as this would act too unevenly; it is done either by oil-burners or by gaseous fuel. The fire-gases first heat the lowest part of the coil, where the tar leaves it and gradually gets to the higher part; after this they serve for superheating the steam, and at last escape through the chimney K.

After starting the apparatus, it takes from ten to eighteen hours before hard pitch is formed; during this time the partially distilled tar is taken back into the hot-tar tank by a pipe.

Only one man is required for working this apparatus, but he must know it thoroughly, since awkward accidents may occur

through leakages of the coil, etc. These can be observed by a number of "sights" in the furnace, and they would also betray themselves by the thick smoke of burning tar escaping out of the chimney. As soon as this happens, the superintendent must at once stop the firing, as well as the tar-pump, and inject superheated steam into the coil by a tap provided for this purpose, which forces the tar out of it in a few minutes; after this the other parts of the apparatus can be stopped, all of this in a very short time. The man must also constantly look after

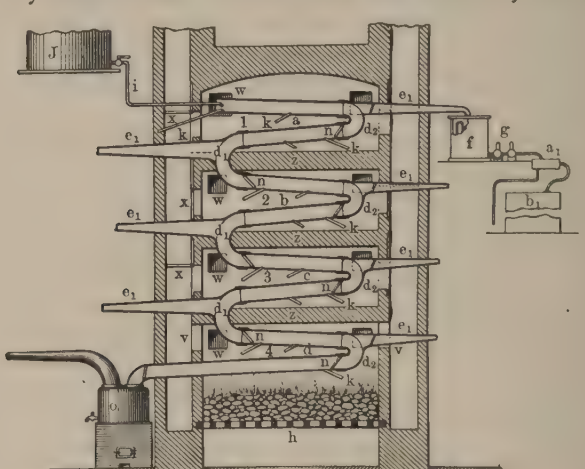


FIG. 118.

the pressure-gauges, fixed in various places, which indicate any plugging-up of the pipes. This happens very rarely, as the vacuum prevents it. One such still was nine months continually at work, without a day's interruption.

One of the stills at the inventor's works can work off up to 150 tons of tar in one day. Almost the only drawback of the system is that the cost of it is high, and does not pay when less than 5000 tons of tar per annum is consumed.

Mason's continuous still (Ger. P. 66097) is primarily intended for petroleum, but is equally applicable to coal-tar. The retort (Figs. 118 and 119) is formed of zigzag pipes, and is composed of as many single chambers (*a*, *b*, *c*, *d*) as there are distillates to separate,

or else of one continuous tract (Fig. 119). The single parts are arranged one over another in a special space of the furnace, (1, 2, 3, 4), divided by partitions (*z*) or flues. e_1 are still-heads, issuing from the bends d_2, *f* coolers, *a* receivers, *g* a vacuum-pump, *b* reservoirs for the products, *h* fireplace, k_1 steam-jacket, k_2 regulating sand-bath. Each chamber can be heated separately, or cooled by flues (*w*) in a methodical way. The oil or tar, contained in J, is introduced through *i* at *a*; a steam-jet (*k*) converts it into a spray, which is repeated in every compart-

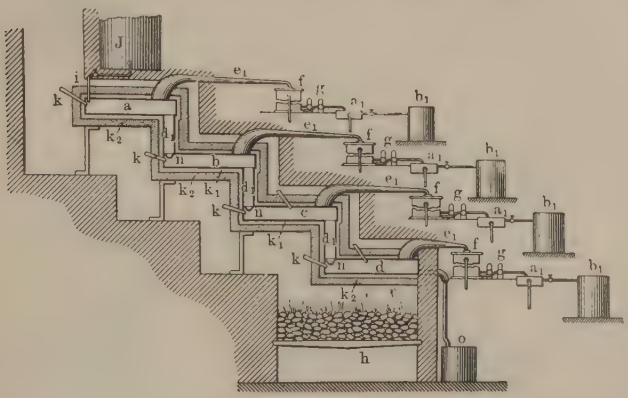


FIG. 119.

ment, the sprayed oil being driven along the hot retort-sides, and the last residue is run into *o*.

Pfropfe's still (Ger. P. 55025, 1890) consists of a semi-cylindrical trough (Figs. 120 and 121), divided by partitions (S) into compartments (A), with communications at *s*. T, inlet for the tar; H, still-heads for each compartment. The pitch runs through *s*, back through the still, and there gives up most of its heat, till it issues at *k*. H. Köhler had the opportunity of working such a still during four months. It had a diameter of 3 ft. 3 ins. and a length of 14 ft., and consisted of eight compartments, each provided with a still-head and cooler. It distilled 3 cwt. of tar per hour, with a consumption of 10 per cent. good coal. Dry steam was blown into the heavy-oil compartments to prevent the formation of coke. The distillation of the first runnings and of light oil was easy, less so the separa-

tion of carbolic oil from creosote oil, but that of the anthracene oil was again better. The pitch-pipe *s* was frequently obstructed,

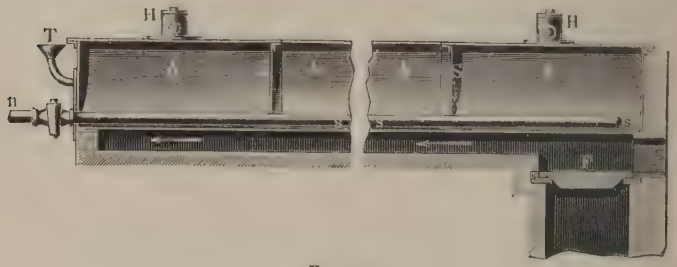


FIG. 120.

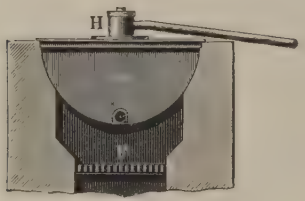


FIG. 121.

and was therefore superseded by running the pitch from the last compartment directly into a closed cooler. The distillation could not be easily carried on in such a manner that the products

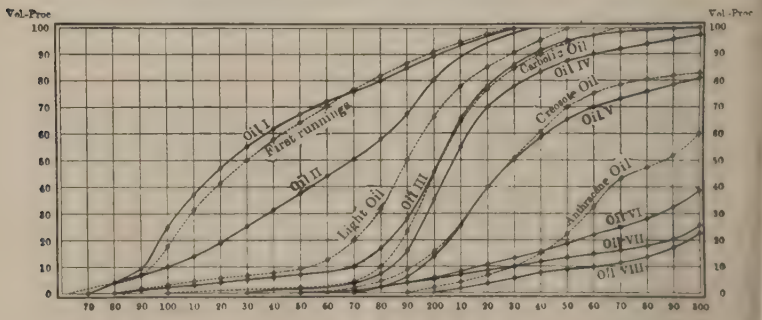


FIG. 122.

were always of even quality, and this would have to be improved by a regulated system of firing. The following curves (Fig. 122) allow a comparison between the results of a Pfropfe still

(dotted line) and those of an ordinary upright vacuum-still (continuous line), which proves that the former are equal to the latter.

There is a certain saving of fuel and of labour. In its present shape Pfropfe's still is best adapted for removing only the water and the more volatile substances, leaving a material well adapted for the manufacture of roofing-felt (p. 280).

The continuous still made by H. Hirzel at Leipzig-Plagwitz

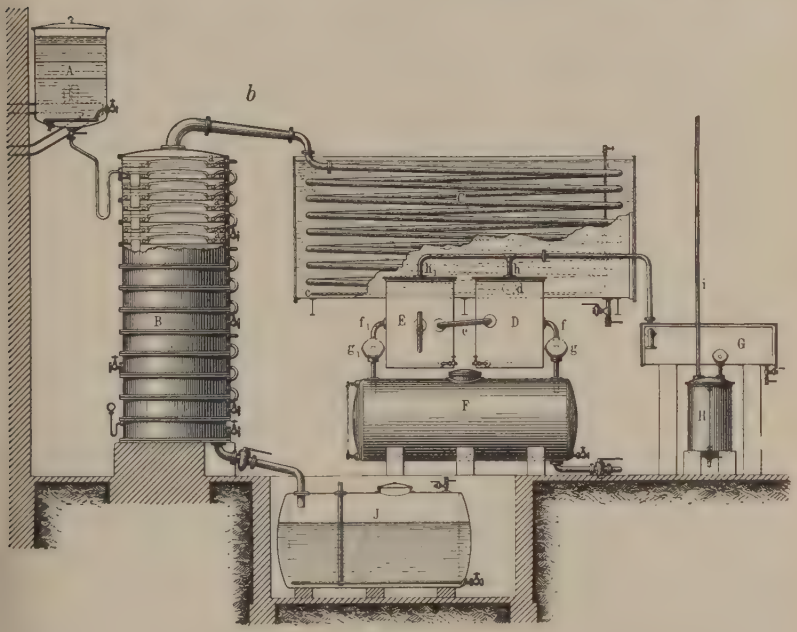


FIG. 123.

(Fig. 123) admits of employing surprisingly low temperatures for distillation. Instead of working up to 300° C., 150° or 160° C. is sufficient, or for anthracene oil and hard pitch 250° instead of 400° and upwards. Thus very pure anthracene is obtained, and the phenols are recoverable most easily in a pure state. The tar is heated up in A, purified from coarse matters by a sieve, and run through a column (B). At the bottom of each of the chambers of this column there is a steam-coil (*a*), which,

when supplied with steam at 90 to 100 lb. pressure, heats the tar to 155° or 160° C. Open steam passes from below to the top and carries off the volatile matters to such a point that at the bottom only soft pitch issues, containing the elements of hard pitch and anthracene oil. The vapours escape through *b* into a cooling-worm (C); at *d* the condensed oils and water run into the separator D, where the heavy oils sink to the bottom; the water and the light oils pass through *e* into a second separator (E), where the water runs off sideways. The tar-oils from D and E run through $f\ f_1$ and $g\ g_1$ into the reservoir F. The contents of the separators D and E are generally warmed up to prevent obstructions by naphthalene, and are therefore provided with pipes ($h\ h_1$) leading the benzol vapours into a supplementary cooler (G) and the receiver H. The soft pitch is collected in the steam-heated pressure-tank J. By working the column at lower temperature it is possible to get at the bottom, instead of soft pitch, a liquid tar, suitable for the manufacture of roofing-felt and as "prepared tar."

The distillate from the usual mode of working contains all the oils boiling up to 300°, all the anthracene remaining in the soft pitch. It can be worked up in the usual manner, but Hirzel recommends the following method:—Cooling down by artificial cold and mechanical agitation, separating the crystallizing naphthalene by a hydraulic press, treating the filtered oil with caustic-soda solution, rectifying the remaining oil by steam, and purifying the distillates by sulphuric acid.

The soft pitch can be worked up as follows:—It is forced from J into a higher-placed reservoir and continuously run into a still heated to 250°, steam superheated to the same temperature being blown in, until the anthracene oil has been driven over; the hard pitch is run off from time to time without any danger or evolution of noxous vapours.

Dr Hirzel's process has been already practically introduced. It is decidedly less dangerous and causes less nuisance than the ordinary stills, but the apparatus is more expensive and requires more supervision. In 1905 Hirzel obtained a new patent (Ger. P. 172224).

Quite recently a continuous tar-distilling apparatus, constructed by Walter Köhn, of Lübeck, is rousing much attention. It is supplied by the Lübecker Apparatebau-Gesellschaft, of

Lübeck, from which I have received the following communications thereon, with permission to publish them, as well as the diagram, Fig. 124. The tar is forced by a pump (*a*) through a series of spiral tubes (b_1 b_2 b_3), heated by a fire or superheated steam, of an aggregate length of several hundred metres. Here the necessary temperature is reached, the velocity of the current of tar being about two metres per second, but the high pressure prevents the formation of gases within the tubes. The heated oil is conducted into the still *c*, where it is throttled by cap *x*, so that it remains under high pressure in the tubes, but on issuing at the cap *x*, which is perforated by many small holes, it is thrown against a baffle plate and is at once converted into a spray, consisting of a mixture of steam and tar oils, which go on to the coolers *d*, *e*, *f*,

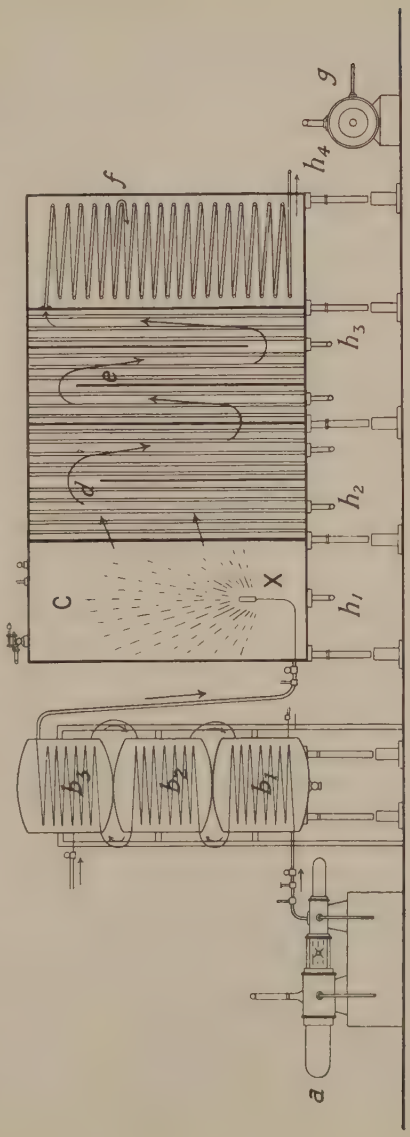


FIG. 124.

whereas the dead oil or pitch runs off at the bottom at *h* into a tank or an ordinary still, to be further distilled The carrying over of liquid pitch into *d'* is prevented by a series of slanting plates. In consequence of the high pressure no coke is formed in the tubes. Where several apparatus are working alongside, the hot pitch may be used for heating the tubes b_1, b_2, b_3. These are kept at different temperatures so that b_1 gives creosote oil, b_2 light oil, and b_3 crude benzol, which goes on for months without any fluctuations of the specific gravities. The cooling may be effected by tar, which is thus pre-heated. According to the duty of the pump and the length of these tubes, a 10-ton still can be filled with dehydrated tar within an hour, but it is best to calculate upon two or three hours. One apparatus is sufficient to supply five stills at 10 tons each, one after the other. The tubes b_1, b_2, b_3 stand a pressure of 250 atmospheres, but are worked only at about 20 atmospheres. There is no danger of fire, even where the heating takes place by coal, as the contents of the tubes are minimal (there is never more than 150 litres of tar in the apparatus) and by the simple turning of a valve the supply of tar is instantaneously stopped. The liquid cannot boil over, as only very small quantities of it are injected per second into *c*. The work is very cleanly and requires no continuous attendance. This system is employed for various purposes; for merely dehydrating tar, for driving out only the lightest oils in order to get "solidified tar" (p. 293), for going as far as "asphalt" (p. 291), soft pitch or even hard pitch, and quite a number of such apparatus are already at work.

Ray, at Turin, in a communication made to the Chemists' Congress at Rome in 1906, describes a continuously working apparatus for distilling tar (patented in Germany as No. 157502), consisting of a battery of horizontal iron retorts, inclined in opposite directions, as they follow one another. The ends of the retorts pass outwards through the brickwork, and communicate by means of pipes. Thus a zigzag is formed, into which the tar enters at one end and the pitch flows out at the other. Each retort is provided with an inlet and outlet valve and a pipe for carrying off the vapours. The heating gas passes first under the last retort and gradually proceeds to the first. The last retort is provided with an inlet for steam, superheated to

250° to 270° C., which facilitates both the escape of the heaviest vapours and the running out of the pitch at a moderate heat, and prevents the formation of coke. It is not necessary to dehydrate the tar before introducing it.

The advantages to be derived from apparatus for a continuous distillation of coal-tar will evidently only come out when very large quantities have to be regularly treated, just as it has been found in the case of petroleum.

Wilton (B. P. 25879, 1907) (*Chem. Zeit.*, 1906, 383) employs for distilling tar in a continuous process two retorts, superposed over one another, and inclined in opposite directions, so that the liquid, entering at the top of the upper retort, leaves the lower cylinder at its lower end. Both retorts are combined with tubular coolers. The tar enters at the bottom of the top cooler, leaves it at the top, enters the bottom of the lower cooler, and leaves this again at the top. In flowing through these two coolers the tar is heated up by the vapours from the top retort, through which it afterwards flows in a thin stream, enters the bottom retorts and flows out at its lower end, the surface being increased by a number of projections attached to the bottom of the retorts. After leaving the bottom retort, the liquid residue flows through the bottom cooler.

Archdale (B. P. 16511, 1902) employs for continuous distillation a steam-boiler-like box, heated outside, with baffle plates on the bottom, forming a zigzag channel, through which the tar flows in at one end and out at the other.

Other patents for continuously acting tar-stills are:—

Werner & Pfleiderer, Ger. P. 106713.

Bockelberg & Sachse, Ger. P. 154755.

Tack, Belg. P. 181041.

Wilke & Co., Ger. P. appl. D16094.

Distillation of Tar for the Purpose of making Illuminating Gas.

The low prices recently prevailing for coal-tar products have led to a proposal to distil the tar in such a way that only those substances are removed which are injurious to the object in question, while all the others, including benzol, are converted into a rich gas. Davis[1] states that gas-tar oils, as well as

[1] *J. Soc. Chem. Ind.*, 1886, p. 6.

petroleum spirits and petroleum residues, become gasified whilst passing over red-hot surfaces, and that about 50 cub. ft. of 50-candle gas are obtained thereby from 1 gall., possessing a sp. gr. of 0·912. Taking the oils as weighing 10·8 lb. per gallon, 1 ton would yield 16,600 cub. ft. of 50-candle gas, approaching very nearly the composition of rich cannel-gas. In order to carry out this process of enrichment on a practical scale (say, for works carbonizing 50 tons of coal per day), a set of three 10-ton tar-stills would have to be provided, so that they might be worked consecutively, one always being run off and refilled. The raw tar is distilled in the usual manner and the distillate conveyed into three separate tanks, A, B, and C, the still being stopped when a sample of the pitch, on being withdrawn, twists easily at a temperature of 55° C., which signifies that it is of very good quality and readily saleable (*cf.* Chapter VI.). The contents of tank A will remain liquid; those of tank B will, on cooling, separate naphthalene, and those of tank C crude anthracene. If tank B is constructed in the form of a filter, the naphthalene can be easily removed, and either worked up, sold, or used as fuel. The oils of tank C must be filter-pressed to recover the anthracene, after which the contents of all are ready to be made into gas. When sufficient oils have accumulated, another of the stills is filled with a mixture from the tanks A and B, and this is slowly distilled, the vapours being passed directly into one end of a through-retort heated to dull redness; the gasified hydrocarbons passing out at the other end by means of the ascension-pipe are mixed with the gas from the ordinary retorts. When four-fifths of the contents of the still have been vaporized, the fire is withdrawn and the still filled up with raw tar, which is distilled as before, and the pitch run out for sale; after which the still is again ready for vaporizing another batch of oils. When sufficient oil from the anthracene has accumulated, it is distilled in whichever still happens to be at liberty. The first fourth is run into the creosote or B tank, the second fourth into the anthracene or C tank, the still being stopped when the pitch will just soften at 50°, when it is run off into the pitch-house in the same manner as when dealing with ordinary tar. In this way any gas-works would be able to supply an illuminating-gas of good quality without the aid of cannel-coal, and to produce pitch and anthracene of the very best quality.

The calculation would run as follows:—

100 tons of ordinary coal give each 10,000 cub. ft. of gas of 17 candles.

5 tons of cannel-coal give each 12,000 cub. ft. of gas of 28 candles.

Coal produce 1000 × 17 candles. . 17,000.
Cannel „ 60 × 28 „ . . 1,680.

In all, 1060 cub. ft. at 17·6 candles.

Taking coal and gas-tar:—

100 tons of coal give 10,000 ft. of 17-candle gas.
2·8 „ tar-oils give 16,000 ft. of 50-candle gas.

Coal produce 1000 × 17 candles = 17,000.
Tar-oils „ 46·5 × 50 candles = 2,325.

In all, 1046·5 cub. ft. at 18·4 candles.

Davis thus makes out that the 7 tons of tar produced from 100 tons of coal [this is much in excess of the average!] has a value to the gas-maker equal to nearly 10 tons of cannel-coal. One through-retort will give about 500 cub. ft. of gas per hour, equal to the decomposition of some 7 gallons of oil per hour.

Davis's statements are altogether contradicted by Lewis T. Wright.[1] He shows that very little is to be gained by incorporating all the benzene of coal-tar with the gas. Taking the percentage by weight of benzol in coal-tar = 0·8, the percentage of tar on the coal as 6·6, and the quantity of gas to be carburetted per ton of coals as 10,000 cub. ft., we have as the total quantity of coal-tar benzol available per 10,000 cub. ft., 0·1183 lb. Since it takes 1·9 lb. of benzol to bring 16-candle gas up to 17 candles, the above quantity of benzol amounts only to an enrichment of 0·06 candle, which is evidently unremunerative. Neither does the dry distillation of tar-oils lead to the solution of the problem. Wright made many experiments, injecting the oils into a retort packed with lumps of caustic lime, kept at an orange-red heat, and passing the gas there generated through a second similar retort. He thus obtained from *crude naphtha* as highest illuminating-power 10,130 cub. ft. of gas of 20½ candles. The greatest yield of gas was 27,100 cub. ft. of 14½ candles; when the yield of gas fell as low as 6000 to 8000 cub. ft. per ton the illuminating-power did not rise above 20 candles. The gas from *light oil* in sixteen

[1] *J. Soc. Chem. Ind.*, 1886., p. 561.

experiments ranged from 18,000 to 30,000 cub. ft. per ton; the illuminating-power from 16 to 13½ candles. The highest illuminating-power obtained with *creosote oil* was 14 candles with a make of 13,300 cub. ft.; the greatest yield of gas 29,300 cub. ft. per ton, with an illuminating-power of 8½ candles. In all these experiments with tar-oils continual stoppages took place from obstinate accumulation of naphthalene in the pipes, which seems impossible to avoid in practice; but, apart from that, the comparatively low yield and the very low illuminating-power of the gas seem to preclude the use of tar-oils for gas-making even at the present low prices. Crude tar, treated as above in retorts charged with lumps of lime, yielded on an average 10,700 cub. ft. of 12½-candle gas; and Wright regards tar as a gas-making material dear as a gift.

Dr Kraemer (priv. comm.) also holds that the treatment of coal-oils for the purpose of illuminating-gas is irrational. In this process but a small proportion of olefins is formed, mostly free hydrogen and hydrocarbons of small illuminating-power, as proved by trials made by the Badische Anilin- und Sodafabrik.

Other Methods for Distilling Coal-tar.

Pfropfe (Ger. P. No. 28838) combines the working up of spent lye from the extraction of sugar from molasses with the distillation of coal-tar. He mixes the spent lye with ground peat and afterwards with coal-tar, and ultimately distils the whole by means of steam. A porous coke remains behind, from which alkali can be extracted by water. This process was tried on the large scale, but the resulting tar-oils were worthless, and the enormous quantity of noxious gases evolved caused the work to be stopped after a very short time. According to another patent of Pfropfe's (No. 96763), tar is mixed with half its weight of sawdust, moulded into blocks, and distilled. The distillate is to be worked up for benzol, etc., on the one hand, and for acetene and acetic acid on the other; the residue is said to consist of pure charcoal. All this appears very doubtful.

Results of Work.

In the case of tars of well-known quality the *duration of the distillation* and the *quantity of the distillates* furnish valuable

indications for changing the receivers. The former must evidently vary much, according to the size and even the shape of the stills. I here quote some of the statements which I have received on this question.

In Paris the distillation of $6\frac{1}{2}$ tons lasts 31 or 32 hours, cooling included. The first runnings and light oil run 14 hours. The necessary fuel amounts to 50 cub. ft. of "agglomerated coke" (patent fuel made from coke breeze).

At a London works a still of 2000 gallons (say 10 tons) capacity is worked off every 24 hours. Fourteen hours are reckoned for the distillation, 10 hours for cooling down, running the pitch, cooling again, and recharging.

Very small stills, of 1200 gallons (= 6 tons) capacity, are all finished in 11 or 12 hours. The fire is slackened an hour after commencing; an hour later the distillation begins, and the heavy oils come over 6 hours after that.

At one German works the horizontal 18-ton stills take 52 hours for working off and 12 hours for cooling. At another the stills (very large, holding 40 to 50 tons) take only from 36 to 42 hours for working off and 6 hours for cooling. At a third works 25-ton stills take 36 hours. At another German works they reckon with 15-ton stills 4 hours to the beginning of the distillation, $19\frac{1}{2}$ hours for light oil, 2 hours for carbolic oil, 1 hour for anthracene oil, and 12 hours till running off the pitch.

At an English works known to me the first runnings from a 22-ton still take 10 hours, the light oil (up to sp. gr. 1·0) 6 hours, creosote oil (including anthracene oil) 12 or 14 hours; cooling down till the pitch is run off, 12 hours. Immediately after, the stills are recharged.

According to Watson Smith, in Lancashire 20-ton stills (steam being employed at the close) were worked off four times per week when anthracene oil was not worked for; in the opposite case, three times per week, or seven times per fortnight. 10-ton stills are worked off six times per week.

In the factories controlled by Dr Kraemer the time of working off their 15-ton stills is 10 to 11 hours, inclusive of charging and of running off the pitch, but only when working with previously dehydrated tar in a continuous way.

In the following tables the *yields* of the different fractions

from coal-tar, from various sources, are given. But these data are not directly comparable one with another, as we have seen that the fractionating is not done in the same way in all.

To simplify matters, I shall at the same time quote the quantity of the final products, wherever they are stated. I shall, however, leave out some of the tables contained in the former editions of this treatise, to make room for more recent data.

Average of my own Results with 1 *ton of Tar from the Midland Counties.*

Ammoniacal liquour	3 gall.
First runnings	5·5 to 8, average 6·33 gall.
Light oil	13·5 to 15 gall.
Creosote oil	68 gall.
Pitch (hard)	11 cwt.

Final Products from the same.

	Average.	Minimum.
50 per cent. benzol	3·30	3·06 gall.
Best naphtha	2·40	2·48 „
Burning naphtha	1·50	1·62 „
Creosote oil directly distilled	68	— „
„ „ „ total	80	80 „
Pitch (hard)	11 cwt.	11 cwt.

Tar from the Berlin Gas-works ("*Chemische Industrie*," 1879, p. 282).

	Per cent.	Per cent.
Benzol (including toluene, etc.)	0·80	
Other colourless oils (higher homologues)	0·60	
Crystallized carbolic acid	0·20	
Cresol for disinfecting purposes	0·30	
Naphthalene	3·70	
		5·60
Creosote oil		24·00
Anthracene (pure)		0·20
Pitch		55·00
Water and loss		15·20
		100·00

The following statements are from *Chemistry, by Writers of Eminence*, Mackenzie, i., pp. 500 and 506.

The average produce from 1200 gall. of tar (about 6 tons) is:—

			Per cent. by weight.
Ammoniacal liquor	about 50 gall.	=	about 4
First light oils	„ 20 „		„ 1·5
Second light oils	„ 20 „		„ 1·5
Creosote oils	„ 250 „		„ 22
Anthracene oils	„ 50 „		„ 4
Pitch	„ 4 tons		„ 67

According to Letheby, 1 ton of gas-coal, as distilled in London, gives about 9 to 10 gall. of tar; 1 ton of coal as distilled in the provinces gives about 15 gall. of tar; 1000 gall. of London tar yield:—

Ammoniacal liquor	20-28 gall., average 24 gall.
Crude naphtha (first light oils)	12-20 „ „ 16 „
Second light oils	4·8-14 „ „ 12 „
Creosote oils	275-296 „ „ 288 „
Pitch	3·2-4 tons „ 3·5 tons

After purification these light oils yield:—

	Gallons.	
40 per cent. benzol	3·44	= 6·84 at 90 per cent.
90 „ „	5·31	
Solvent naphtha	4·18	
Last runnings	1·2	
Total dead oils	301·87	

A. J. Dickinson gives as the average yield from 1000 gall. of London tar:—

	Gallons.	Per cent. by volume.
Naphtha (containing 6 per cent benzol)	30	3
Ammoniacal water	30	3
Anthracene (at 25 per cent.)	10	1
Pitch	650	65
Creosote, lubricating-oils, carbolic acid	280	28

The figures given by Letheby and Dickinson are somewhat different from the following, given on oath, in the course of a lawsuit, as the average yield of London tar (supplied to me by the kindness of Mr S. B. Boulton). The first column represents the results obtained at the Silvertown works of Messrs Burt, Boulton, & Haywood; the second, those obtained at the Beckton works of the Gas-Light and Coke Company (these two

being among the largest tar-distillers in the world). In the first column all the oils are dehydrated and the water is included in the percentage of ammoniacal liquor :—

	Silvertown.	Beckton.
Ammoniacal liquor	4·16	2·00
Crude naphtha	1·50 of 45% at 120°	1·66 of 30% at 120°
Light oil	1·16	1·62
Creosote (containing naphthalene)	14·16	15·70
Anthracene oil (strained or green oil)	14·00	18·83
Anthracene, 300 per cent.	1·80	1·90
Pitch	60·00	56·29
Loss	3·22	2·00
	100·00	100·00

Watson Smith obtained in 1869, from Lancashire tar [mostly made from cannel-coal], as follows. One thousand gall. of tar of sp. gr. 1·16 = 5·3 tons, yield :—

		Per cent. by weight.
Ammoniacal liquor (4 per cent.)	25 gall.	= 2·2
First light oils	28 „	= 2·2
Second light oils	131 „	= 10·6
Creosote oils	87 „	= 7·6
Anthracene oils	191 „	= 16·9
Pitch	3¼ tons.	= 60·5

On further rectification these distillates yield :—

90 per cent. benzol	about 6 gall.
Solvent naphtha	„ 74 „
Carbolic acid	„ 6½ „
30 per cent. anthracene	„ 0·50 cwt.
Equal to pure anthracene	„ 0·15 „

According to Watson Smith, the richest and best tar comes from small gas-works, because at those works the greatest possible yield from the coal is not, as at the large works, a primary consideration. There are contractors who drive about the country buying up such small lots of tar and gas-liquor, and taking them to the tar-distillers for sale.

Compare also the results obtained by Köhler, quoted p. 361.

The following table, compiled by Sir Henry Roscoe from statements collected by Messrs Watson Smith and I. Levinstein, represents the average yield of products from Lancashire tar,

together with some interesting statements concerning the dyeing-power of the artificial colours derived therefrom :[1]—

One ton of Lancashire Coal yields, when distilled in Gas-retorts, on an average:—

Gas (cubic feet).	Ammoniacal liquor, 5° Tw.	Equivalent to Ammonium sulphate.	Coal (gas) tar, sp. gr. 1·16.	Coke.
10,000	20 to 25 gall.	30 lb.	12 gall. = 139·2 lb.	13 cwt.

Twelve gallons of Gas-tar yield (average of Manchester and Salford Tar):—

Benzene.	Toluene.	Phenol proper.	Solvent Naphtha for Indiarubber, containing the three Xylenes.	Heavy Naphtha.
Lb.	Lb.	Lb.	Lb.	Lb.
1·10 = Aniline 1·10.	0·90 = Toluidine 0·77		2·44 yielding 0·12 Xylene = 0·07 Xylidine.	2·40
= Magenta 0·623 or 1·10 lb. Aniline yield 1·23 lb. Methyl Violet.		Aurin 1·2		

Naphthalene.	Creosote.	Heavy Oil.	Anthracene.	Pitch.
Lb.	Lb.	Lb.	Lb.	Lb.
6·30 = α Naphthylamine 5·25 = α or β Naphthol 4·75 = Vermilline Scarlet, RRR. 7·11, or = Naphthol Yellow * 9·50	17·0	14	0·46 Alizarin 20% 2·25	69·6

* The naphthol yellow is a representative colour from α naphthol, while the vermilline scarlet is a representative colour from the combination of α naphthylamine with β naphthol.

[1] Lecture delivered at the Royal Institution, 16th April 1886, p. 7.

Dyeing-powers of Colours from 1 *ton of Lancashire Coal.*

Lb. 0·623 Magenta dye 500 yards 27 inches wide Flannel a full shade.	or	Lb. 1·23 Methyl Violet dye 1000 yards 27 inches wide Flannel a full Violet.
Lb. 9·50 Naphthol Yellow dye 3800 yards 27 inches wide Flannel a full Yellow.	or	Lb. 7·11 Vermilline dye 2560 yards 27 inches wide Flannel a full Scarlet.
Lb. 1·2 Aurin dye 120 yards 27 inches wide Flannel a full Orange.		Lb. 2·25 Alizarin 20% dye 255 yards Printer's cloth a full Turkey Red.

Dyeing-power of Colours from 1 *lb. of Lancashire Coal.*

Magenta	or	Violet	Yellow	or	Scarlet
a piece of Flannel 8 in. by 27 in.		a piece of Flannel 24 in. by 27 in.	a piece of Flannel 61 in. by 27 in.		a piece of Flannel 41 in. by 27 in.

Orange	Turkey Red
a piece of Flannel 1·93 in. by 27 in.	a piece of Flannel 4 in. by 27 in.

According to a prospectus issued in 1896 by the Badische Anilin- und Sodafabrik, 1000 kg. coal yield 50 kg. tar, and these again yield: 0·4 kg. benzols (=0·3 kg. magenta or 0·5 kg aniline blue); 0·3 anthracene (=0·3 alizarine or 0·3 alizarine blue); 1·0 naphthalene (=0·35 kg. indigo).

The following statistics have been kindly supplied to me by Mr Wilton, manager of the Beckton tar-works, as

representing the production of the United Kingdom in 1885 :—

	Gallons	= Tons.
Ammoniacal liquor from tar alone	3,600,000	1,200 (of sulphate).
Carbolic acid (crude)	600,000	
Creosote oil	21,600,000	
Of this there was liquid creosote	10,800,000	
„ „ creosote salts (= crude naphthalene)		56,620
corresponding to pure naphthalene		25,310
Green oil	24,000,000	
Benzol and toluol	1,500,000	
Solvent naphtha	620,000	
Anthracene (pure) = 6,840,000 units =		3,420
Pitch		396,000

Total quantity of tar distilled 120 million gallons; say 645,000 tons.

A statement in the *Chem. Zeit.* (1879, p. 148) puts the yield from 11,250 litres (= 10 tons) of London tar at :—

50 per cent benzol	12·96 litres	=	1·1 per cent.
Solvent naphtha	12·15 „	=	1·0 „
Burning naphtha	16·75 „	=	1·4 „
Creosote oil	373·5 „	=	35·0 „
Anthracene cake (30 per cent.)	11·25 „	=	1·0 „
Pitch	5870 kg.	=	58·6 „

According to Häussermann (*Industrie der Theerfarbstoffe*, 1881, p. 13), 100 parts of tar from German coals yield

5 to 8 per cent.	light oil,
25 „ 30 „	creosote oil,
8 „ 10 „	anthracene oil,
50 „ 55 „	pitch.

The final products are

0·6 per cent.	benzene,
0·4 „	toluene,
0·5 „	higher homologues,
8 to 12 „	pure naphthalene,
5 „ 6 „	phenol,
0·25 „ 0·3 „	anthracene (pure).

According to G. Schultz (*Chemie des Steinkohlentheers*, 2nd

ed., vol. i., p. 67), there were obtained, in a Rhenish tar-works, from 100 parts of tar :—

	Per cent.
Purified benzol (for aniline and as a detergent)	1·00
Pure anthracene	0·33
Pure naphthalene	2·00
Creosote oil	30·00
Pitch	60·00
Ammoniacal liquor	2 to 10·00

Kraemer and Spilker[1] make the following statements, founded on the results of a number of the largest German tar-works. Heavy tars, with 25 per cent. and upwards of carbon, and sp. gr. over 1·21, yield from 32 to 35 per cent. oily distillates. Normal tars, of sp. gr. 1·16 to 1·20, yield 38 to 40 per cent. oils, lighter coke tars 42 per cent. and more. At four German factories, working with different raw material, but otherwise exactly under the same conditions and with the same apparatus, the following results were obtained :—

No. I. Worked tar from Silesian gas-coal.

No. II. Tar from gas-works, where much Saxon coal and paraffinoid additions were used.

No. III. Tar from the coast, where mostly English coal is used.

No. IV. Tar from Saar coals, with addition of paraffinoid coal.

Results of Distillation per cent.

No.	Water.	Pitch.	Total oils.	Light oil, 0·910-0·950.	Middle oil, 1·01.	Creosote oil, 1·04.	Anthracene oil, 1·10.
I.	3·0	55·1	41·3	2·1	12·0	9·2	18·0
II.	4·9	52·2	41·8	2·5	12·9	11·1	15·2
III.	3·1	59·9	37·0	3·3	9·4	7·0	17·0
IV.	4·1	59·4	35·0	3·8	10·8	8·6	12·1

The yield from normal tars may be taken as follows :—

	Sp. gr.	
Light oil	0·910 to 9·50	2 to 3 per cent.
Middle oil	1·01	10 „ 12 „
Creosote oil	1·04	8 „ 10 „
Anthracene oil	1·10	16 „ 18 „

[1] Muspratt-Stohmann's, *Techn. Chemie*, 4th ed. (1905), vol. viii., p. 14.

Coke-tars do not materially differ from gas-tars. On the whole they yield less benzol and phenols, but rather more anthracene. Oil-gas tars, however, possess quite a different character, corresponding to the paraffinoid nature of the raw material. They yield no phenols and very little pyridines, and the oils contain much less aromatic compounds. Oil-gas benzol always contains much olefins: the middle oils contain but little naphthalene, and the heavy oils hardly any anthracene, which is, moreover, contaminated with methylanthracene, etc. *Blast-furnace tars* occupy an intermediate position between coal-tars and oil-gas tars.

Petersen-Kündig[1] makes the following statements, referring to a 5-ton still.

1. *Stage (before any distillate comes over).*

Coal used for firing (without vacuum), 60 kg. Time required from lighting the fire to the commencement of distillation, 2 hours. The pumping lasts 2 hours, and the firing is begun ¾ hour before the pumping is finished.

The thermometer in the exit-pipe shows 70° C. when the distillation begins.

2. *Light Oil Stage.*

Coal used (if the vacuum is started from 130°), about 160 kg.; without vacuum, 168 kg. Duration, about 5 hours. Temperature, between 70° and 206° C. Specific gravity of oil coming over on the average, 0·96; at the end, 1·0 at 20° C. Cooling-water used, about 890 litres; at the end its temperature should be 65° to 70° C.

3. *Carbolic Oil Stage.*

Coal used: with vacuum, 38 kg.; without, 43 kg. Duration, about 1 hour. Temperature, between 206° and 270° C. Specific gravity of oil, 1·015 at 15°; in the end, 1·029 at 20°. Cooling-water used, about 270 litres; should be in the end 78° to 80° C.

When distilling for "refined tar," stop at 210°; or else to 240°, in order to obtain carbolic acid, but in this case the residue must be diluted with heavy oil.

[1] *Wie eine moderne Teerdestillation, etc., eingerichitet sein muss*, p. 60.

4. *Heavy Oil Stage.*

Coal used: with vacuum, 30 kg.; without, 38 kg. Duration, $1\frac{1}{4}$ hour. Temperature, between 240° and 264° C. Sp. gr. of oil, 1·035 at 15°; in the end, 1·045 at 20°. Cooling-water, 340 litres, of 85° C. in the end.

5. *Anthracene Oil Stage.*

Coal used: with vacuum, for soft pitch, 40 kg.; for hard pitch, 35 kg.; without vacuum, for soft pitch, 46 kg.; for hard pitch, 65 kg. Duration, for soft pitch, 70, for hard pitch, 95 minutes. Temperature for soft pitch 264° to 296°, for hard pitch 264° to 315° C. Sp. gr. of oil on the whole, 1·055 at 15°; in the end, 1·07 to 1·08. Cooling-water, 320 litres for soft pitch, 430 litres for hard pitch; its temperature at the end is = 86° to 87° C.

Altogether, for a 5-ton still—

When distilling for soft pitch, with a vacuum, 328 kg. coal; without vacuum, 355 kg. For hard pitch, with a vacuum, 343 kg.; without, 374 kg. Duration from lighting the fire, 10 hours 25 minutes for soft pitch, 10 hours 50 minutes for hard pitch. Cooling-water used for soft pitch, 1820 litres; for hard pitch, 1930 litres.

The yields from *coke-oven tars* have been quoted on pp. 112 *et seq.*; from *water-gas tars*, pp. 140 *et seq.*

Testing of Tar in the Laboratory.

If a sample of tar has to be tested for its yield on a smaller scale, its distillation must be carried on in exactly the same way as on the large scale. The result will be all the more reliable the larger the scale of the testing-operation. When distilling, say, 10 gall., the results will be only approximative, especially for benzol and naphtha. It is better to employ small stills holding 80 to 100 gall.; but it is even preferable to distil 200 to 250 gall. from a light oil still (Chapter X.). The products are respectively weighed and measured; and light oil and naphtha are tested for their yield of benzol and naphtha according to the rules given at the close of Chapter XI.

Where the testing of tar must be performed with ordinary laboratory appliances, the following hints, by Watson Smith,[1]

[1] *J. Soc. Chem. Ind*, 1883, p. 496.

will be found extremely valuable, and are therefore quoted *in extenso*:—

"It is well known to those who have attempted the distillation of samples of coal-tar (wood-tar is just as difficult to manage), that, owing to the invariable presence of water, often in considerable amount, there is extreme difficulty in the earlier stage of the process in preventing boiling or frothing over of the contents of the retort. Sometimes disproportionately large iron retorts are used for such trials of small quantities of tar, in order to leave as much room as possible for frothing up. By the method about to be described, we have used, in the laboratory of the Owens College, only large glass retorts, holding about 2½ litres, when filled to within ¾ of an inch of the beak of the retort, and have found no difficulty in fractionating the tar in such apparatus, when the proper precautions were observed. The following are the salient points in the method I have devised:—

"The tar is first freed from water as much as possible, by placing the containing vessel (*e.g.*, a large glass beaker) in hot water, and allowing to stand for about a day and night, the beaker being well covered with a glass plate. The reduction thus effected of the density and tenacity of the tar allows of the separation of water with greater facility. If the tar be heavier than water it settles down, and the water rises, forming a layer, which, after allowing to cool, may be decanted off. Frequently a great deal of water may be got rid of by inclining the vessel alternately in different directions, when, if the tar be a heavy one, the water collects and flows to the point of inclination more rapidly, and so the portion accumulated may be decanted off before the tar reaches that point. In the case of a tar or tar-oil lighter than water, a subnatant layer of water forms by the warming and settling process; and in this case a tolerably wide siphon or run-over might be used, or, from a beaker, the tar-oil might be merely decanted." For the *specific gravity determination*, "a measured quantity of tar (say 1 litre), settled or partially dehydrated as above, is run into a previously tared vessel, and, after cooling to 15° C., the latter, with its contents, is weighed. These data are sufficient for the specific gravity. The ordinary specific-gravity bottle would be a clumsy contrivance in this case. For the *distillation* about 2½ litres of tar were taken and poured into a large glass retort arranged on a stand in the

usual way. The stand is placed in a large iron tray with high sides (about 6 to 7 ins.), the bottom of which is covered with sand to the depth of ½ an inch or so. This arrangement is to afford protection to the operator, in case of accident. A glass tube, besides the thermometer, is inserted through the cork acting as a stopper. This tube is drawn out to a small aperture, and is caused to dip about half-way to the bottom of the retort from the surface of the tar. A slow current of air is passed through the tube and forced through the tar, and the temperature of the tar is carefully and not too quickly raised to from 60° to 70° C. This temperature is maintained, if necessary, for a day or two, until all ammonia-water is expelled. If the tar be a heavy one, a layer of ammonia-water may form on its surface after heating to 60° to 70° for some time. If the layer be of considerable thickness, it will be advisable to remove the stopper and decant it off. Frequently a slow distillation for about a day or more may thus be spared by an operation lasting a few minutes only. If the tar contain much spirit or benzol, the receiver, which should be one with a second opening admitting a cork, is connected with a wash-bottle containing some heavy oil, to retain naphtha vapours else carried off by the air-current. The naphtha is afterwards recovered by blowing wet steam through the oil, the vessel being connected with a condenser. The volume of the naphtha is then measured. When all water is removed from the tar, the distillation will proceed quite smoothly."

I may also be allowed to quote my own directions for testing tar in the laboratory, as given in the *J. Soc. Chem. Ind.*, 1887, p. 581 :—

"Such an investigation cannot be expected to yield useful results, unless somewhat large quantities are taken in hand. But in a scientific laboratory it is difficult to employ more than a few kilograms for each distillation. The results thus obtained will never exactly coincide with those obtained in manufacturing practice, but experience proves that they give a very good idea of the general quality of the tar. It would be most convenient to employ for such quantities distilling vessels made of metal, and I would, indeed, strongly recommend this for factory laboratories, all the more as it is thus easy to work upon very much larger quantities. But in scientific laboratories,

where, for more reasons than one, it is out of the question to distil a hundredweight of tar or some such quantity, it will be always preferred to accurately observe the progress of the operation, and this it is only possible to do in glass retorts. Especially the dehydration of the tar, such as will be described further on, can be hardly carried out in any other way, whilst it is comparatively easily done in glass retorts. Watson Smith has also used such for his investigations.

"My retorts were tubulated, holding about 5 litres, and were heated in a kind of sand-air bath—that is, in a suitably-shaped thin wrought-iron dish, the bottom of which was covered by a layer of sand 1 cm. thick. About half of the retort was within the dish, and the whole of it, down to the sand, and including the upper part of the neck, was wrapped round with wire gauze. The heating was done by a Fletcher's gas-stove, placed in a large flat pan, partially filled with sand. Hence, in case of an accident, the tar would have first run into the upper pan, forming the sand-air bath, and anything boiling over from this would have been caught in the lower pan.

"The tubulure of the retort was fitted with a twice-perforated cork, holding a thermometer and a tube, drawn out into a capillary at the lower end, with the object of passing a minute current of air-bubbles through the liquid, in order to prevent bumping. This precaution, first introduced by Dittmar, and also employed by Watson Smith, was found to be very useful indeed; but it seems possible that the air-current might carry away a minute quantity of benzene.

"The retort was, during the first part of the operation, connected with a Liebig's condenser, so long as the distillate remained entirely liquid. When it began to partly solidify—that is, between 170° and 180°—the cooler was removed; and since now the last portions of water had been volatilized, and no more bumping was to be apprehended, the current of air was discontinued. The last of the water escaped between 140° and 170° with explosive violence.

"The distillation of 2½ or 3 litres of tar took about eight hours.[1] It is decidedly advisable to carry it right through

[1] According to Kraemer (priv. comm.) this period can be considerably shortened by first filling the retort only about a quarter, and then gradually running in the other portion; this prevents any frothing-over.

without any interruption, both because the heating-up, after the contents of the retort have been semi-solid or solid on cooling, is always an awkward operation, and because during the cooling-down and the heating-up a considerable quantity of substance passes over far below the proper boiling-points.

"The distillates were collected in tared, narrow, graduated cylinders, and after cooling down they were measured and weighed. The fractions were made in the way to be stated below. But although, as a matter of course, every precaution was taken to keep the temperature as constant as possible, still, without any recognizable reason, the thermometer showed considerable oscillations, and sometimes went down 20° without any diminution in the rate of distillation.

"It cannot be said that such assays are exact analytical operations. The fractions will differ to some extent, as the distillation proceeds more or less slowly. Each time, when substances are poured from one vessel into another, small losses are unavoidable, although in the case of the higher-boiling substances the vessels were rinsed with ether, which was subsequently evaporated. In washing and drying, in the case of the first distillates also by evaporation, small losses will occur, which become all the more important when the absolute quantity of substance is only slight.

"If the tar has not been previously dehydrated, the work must begin with that operation, which is of great importance. It is not feasible to go as far as 100°, because then the tar would lose many valuable portions, especially as the operation takes so much time. Hence, the dehydration was performed in the retort itself, turning its neck upwards and connecting it with a cooler, inclined downwards, in order to collect any benzene escaping along with the water. The heating was continued in this manner to 60° to 70° for a full fortnight; every morning, before recommencing, the water collected in the meantime on the surface was removed by a pipette. For all that some water remained behind, evidently in chemical combination with phenol, pyridine, etc., and this could only be removed by distillation.

"The fractions were made as follows:—

1. Light oil, up to 170°.
2. Middle oil, up to 230° (carbolic oil).

3. Creosote oil, up to 270°.
4. Anthracene oil, up to the close of the distillation, which was continued as long as anything would come over; this explains why the pitch was extraordinarily hard.

"The above fractions were treated in the following manner:—The *Light Oil* was first agitated with caustic soda solution of sp. gr. 1·1, and the contraction of volume was calculated as 'phenols.' The oil was then washed with water, with concentrated sulphuric acid, and again with water, and the total contraction was calculated as 'loss by washing.' The residual oil was distilled, and the fractions coming over up to 100° and 140° were separately collected. The distillate up to 140° was considered as 'crude aniline benzol,' and its degree of purity was examined by nitrification with the ordinary mixture of acids. The portion remaining behind at 140° was calculated as 'heavy naphtha': it must, of course, leave a good deal of residue on rectification, and this residue will practically go to the creosote oil; but, on the other hand, some heavy naphtha will come back from the 'middle oil,' and on the small scale it was impossible to say how far this would compensate for the residue left on rectifying. The small quantity of liquid also made it impossible to separate the 'aniline benzol' into benzene, toluene, and xylenes.

"From the *Middle Oil* and the *Creosote Oil* a quantity of naphthalene crystallized on cooling. This was filtered through calico, strongly pressed, and calculated as 'crude naphthalene.' The liquid portion of the oil (making allowance for the mechanical loss in pressing) was treated with caustic soda solution, and the contraction of volume again set down as 'phenols.'

"The *Anthracene Oil*, after cooling, was filtered through calico, the crude anthracene was pressed cold, then spread out upon porous earthenware slabs, heated in an air-bath to 30° to 40°, pressed while warm, and weighed. It was now analysed by the 'Höchst' test; but since in the trade anthracene is usually sold as 30 or 40 per cent., three times the weight of pure anthracene was deducted from the weight of crude anthracene oil, to get at the figure for liquid anthracene oil.

"The *pitch* was tested for its softening point by heating a

piece of the size of a pea on a wire in an air-bath beside a thermometer until, by pressing with the fingers, it proved to be distinctly plastic. The water-bath did not suffice for this purpose. It was further tested for 'carbon'—one of the most tedious parts of the work. For this purpose it was extracted alternately with boiling benzene and carbon disulphide; but it took many days' toil; the solvents did not show any but a faint colour, and left no more residue when evaporated on a watch-glass. This operation must be carried out with the greatest caution, since otherwise fine particles of carbon will pass through the filter; for this reason Soxhlet's extracting apparatus, otherwise so convenient, could not be employed."

Rispler[1] describes an apparatus by means of which 5 or 6 kg. of tar may be freed from water and light oil within an hour. It is an iron cylinder, holding the required quantity, with an arched top and two necks. One of these, in the centre, is closed by a glass T-piece, in which a thermometer is placed on the top, while the lateral branch, which is slightly inclined downwards, is connected with a Liebig's cooler and receiver. The second neck of the still top is fitted with a tap, and above this a funnel, holding 1½ kg. tar and heatable by steam or hot water. The still itself is heated by a large circular burner. Weigh off 5 to 6 kg. tar; pour 1½ kg. into the funnel, which in the case of viscous tars must be heated; run about half of this into the still and heat this gradually. When the thermometer indicates 110° to 120°, run more tar into the still quite slowly, and allow the temperature to rise gradually to 130°, at which it is kept until all the tar has run in. The regulation of the distillation is facilitated by the play of the vapours in the glass T-piece. After all the tar has run in and all the water and light oil are distilled off, the tap is closed and the distillation finished in the usual manner. If only the water is to be estimated, the still is fitted with a lateral tap a little above the bottom, through which the dehydrated tar is run off. Now the next sample is gradually run in. In this manner 5 or 6 estimations of water can be made in one day. This apparatus is sold by the firm Vereinigte Fabriken für Laboratoriumsbedarf, Berlin, N., which also supplies a similar apparatus, constructed by R. Kuhn and described in *Z. für chem. Apparatenkunde*, Oct. 1905.

[1] *Chem. Zeit.*, 1905, 488.

Special Tests for Coal-tar.

The specific gravity of tar cannot be estimated by means of an ordinary specific-gravity bottle, which is too difficult to fill exactly and to clean in this case. I have (*Z. angew. Chem.*, 1894, p. 450) described a "weighing-bottle" of the shape shown in Fig. 125 with a glass stopper provided with a rill, *a*, 2 mm. wide. The operation is performed, as when estimating the specific gravity of solids, by filling the glass only partially with tar and then completely with water. First the glass is weighed empty (*a*), and again after filling it with water of 15° C (*b*). It

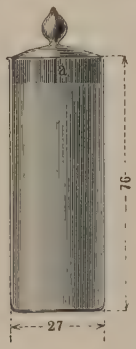


FIG. 125.

is then dried, tar is poured in up to about two-thirds of its height, and the glass, without its stopper, is placed for about an hour in hot water, till all air-bubbles disappear. After cooling, the weight of the glass plus the tar is determined (*c*). Now water is poured in, the stopper is inserted, the water issuing from the rill is removed, the whole is allowed to stand in a vessel filled with water of known temperature, and the weight is again taken (*d*). The specific gravity (*s*) sought is:

$$s = \frac{c-a}{b+c-(a+d)}.$$

In most cases the specific gravity of tar, after dehydration, is a sufficient guide as to its quality. According to Köhler (*Z. angew. Chem.*, 1888, p. 677), it depends mainly upon

the percentage of free carbon, as shown in the following table :—

Origin of tar.	Spec. grav.	Free carbon per cent.
Heidelberg	1·220	23·75
Darmstadt	1·215	20·93
Baden-Baden	1·195	19·92
Bockenheim	1·190	18·24
Frankfort	1·180	15·70
Bamberg	1·175	15·15
Neustadt	1·172	15·07
Caunstadt	1·164	14·05
Rottweil	1·161	14·00
Karlsruhe	1·155	13·50
Ulm	1·150	12·44
Heilbronn	1·150	12·42
Oos	1·145	5·00

The estimation of free carbon (cf. *supra*, pp. 241 and 321) in tar is decidedly important. Kraemer extracts the tar with forty times its weight of xylene. Köhler considers it more expeditious to heat 10 g. tar with a mixture of 25 g. glacial acetic acid and 25 g. toluene, pouring the liquid on to two filters of equal weight, placed one within the other, and washing with boiling benzene until this runs off colourless. After drying, the outer filter is used as tare in weighing the inner.

Kraemer and Spilker recommend the following methods as the simplest for factory use. Mix 1 g. tar with 5 g. aniline and pour into a cup of porous porcelain of this shape: |———| which absorbs the liquid portion, leaving the carbon as a leaf-like mass which can be detached by means of a wooden spatula, put into a tared watch-glass and weighed after keeping in the water-bath for a few hours. The results show 2 or 3 per cent. less carbon than is obtained by Kraemer's xylene method, but are quite useful for comparative purposes.

Hodurek (*Oest. Chem. Zeit.*, 1904, p. 365) has found that the various solvents, especially benzene, glacial acetic acid, and ether, have a precipitating effect on bituminous substances, especially those contained in coal-tar pitch. If the latter is dissolved in the least possible quantity of benzol, the filtered solution on addition of an excess of benzol yields brown or

reddish brown substances—just those which give to carbolineum (cf. *infra*) its characteristic colour. He therefore proceeds as follows for the estimation of free carbon in tar (and pitch). He mixes 5 g. tar with 200 c.c. 90 per cent. benzol, heats for 5 minutes to boiling, filters on to a dry, weighed paper filter, washes with 100 c.c. boiling benzol, dries at 100° C., and weighs. Thus he finds carbon and bitumen. In a second portion of the tar the suspended carbon is removed by careful filtration through paper and 5 g. of the filtrate are treated as above; the difference of both estimations yields the percentage of free carbon.

The more free carbon, the more viscous the tar, and the more easily will it froth over during the distillation. Tars containing less free carbon, that is, of less specific gravity, are richer in benzene and other light hydrocarbons than those containing more free carbon. But this holds good only to a certain limit, say, 15 or 17 per cent. free carbon. Above this tars of equal percentage of free carbon may furnish either more anthracene or more benzene, etc., according to their origin. But if they contain considerably more carbon than 17 per cent., they are sure to yield less valuable products of all kinds and more pitch.

If K is the percentage of free carbon in the pitch and k the percentage of free carbon in the tar, the yield of pitch is $\frac{100\,k}{K}$. Moderately hard pitch contains about 28 per cent. free C; for normal tar with 16 per cent. we thus find a yield:

$$\frac{100 \times 16}{28} = 57 \text{ per cent.},$$

which is in sufficient agreement with experience.

The estimation of water in the tar has to be performed much more frequently than other tests of it, and it has been referred to in several of the foregoing descriptions of work. Payne[1] employs for this purpose a small copper still of cylindrical form, holding one litre. The upper end is surrounded by a heavy turned flange, the lid is of brass and clamped to the still by a single clamp passing over the top, a paper gasket being placed between the two metal surfaces. The condenser consists of an

[1] *J. Amer. Chem. Soc.*, 1903, xxv., p. 814.

open trough, through which passes a slanting glass-tube 27 ins. long (a Liebig's condenser). Great care must be exerted in taking the sample, preferably by means of a small cock through which a small stream is allowed to flow during the pumping of the tar into or out of the boat, car, etc. The quantity thus obtained must be violently stirred and at once fitted into wide-mouthed quart bottles or cans, before any separation can take place. Five hundred c.c. of this sample are put in the still, the lid is securely clamped and the Liebig's tube and thermometer fixed in their places. The heat must be applied very carefully, to avoid bumping and foaming over, preferably by a ring burner, which is at first placed so that the top of the still is heated; it is gradually lowered, and, in the end, an additional burner may be placed under the bottom. To be certain that all water is expelled, the thermometer in the vapour should reach 200° C. Oil and water are collected; they separate at once and the c.c. of water are read off. If desired, the distillation can then be carried on until the end. Some tars are very difficult to free from water, the contents of the still boiling over in spite of all precautions. This may be avoided by adding to the tar a hydrocarbon boiling slightly higher than water, *e.g.* toluene. This thins the tar and carries over the water completely and very rapidly.

The just-named process (addition of 40 to 45 per cent. benzol to tar containing much water, in order to prevent frothing over) had been previously practised by Maywald,[1] and also from the subject of a previous patent for treating petroleum.

The methods for estimating the water in tar published by Becker[2] and Senger[3] are quite similar to that of Payne.

The apparatus of Rispler (*supra*, p. 424) can also be of service for this purpose, and seems to be mostly employed for estimations of water in tar.

[1] Ahrens, *Chem. techn. Analyst*, p. 211.
[2] *J. Gasbeleucht.*, 1902, 764; *Chem. Centr.*, 1902, ii., 1279.
[3] *Ibid.*, 1902, 841; *ibid.*, p. 1435.

CHAPTER VI

PITCH

It need hardly be said that the word "pitch" denotes many substances which have nothing to do with coal-tar, such as pitch from petroleum, wood, natural bitumen, and some products obtained in the manufacture of stearine, wool, etc. Donath and Margosches (*Chem. Ind.*, 1904, 221) discourse on these various descriptions of pitch and asphalt and their distinctions from coal-tar pitch. In this book we treat exclusively of the latter.

The nature of coal-tar pitch is very little elucidated up to the present. We shall presently quote statements on the ultimate analysis of pitch, and on the amount extracted by various solvents, but this evidently does not lead to a knowledge of the chemical compounds constituting the pitch. Aug. Lemoine, in a pamphlet published in 1902 under the title, *Sur la connaissance des brais minéraux* (Charleroi), contends that coal-tar pitch is a mixture of carbon, of "carbures," and "carbenes." About the so-called "carbon" we shall presently say more; all are agreed that it contributes nothing to the plastic and agglutinating properties of the pitch. The "carbures" are at the ordinary temperature a brownish green or black mass, like butter, entirely fluid at 45° to 50° C.; they impart to the pitch its plasticity and its power to glue together pulverulent substances into solid masses. The designation of "carbenes" has been given by Lemoine to a black, crystalline, shining powder which he found in pitch, softening and fusing about 200° C. At that temperature it swells up and spreads on the glass, adhering to it but slightly. The chemical nature of these compounds varies very much, but anyhow they are

non-saturated compounds, as they combine with bromine. They impart to the pitch the property of being solid at ordinary temperatures; they contribute but little to its agglomerating properties, but they are indispensable, because without their presence the tar would be too glutinous; the briquettes, etc., would adhere to the moulds, and would be too soft and easily deformated; but if there is too much of them, the briquettes would be too little compact. Lemoine gives some tables on the percentage of agglutinating substances in various pitches, and on their degree of plasticity, but as he does not indicate how his results are obtained, we abstain from going into his figures.

Kraemer (*Chem. Ind.*, 1903, 303) develops his ideas on the formation of coal-tar pitch. Certain non-saturated compounds—*e.g.* indene—are polymerised and subsequently decompose by heating, the hydrogen changing its position within the molecule. On one side one molecule of hydrindene, containing 2H more than indene, is formed, on the other side truxene, which contains 6H more than indene and has a high melting-point:

$$4C_9H_8 = 2C_9H_{10} + C_{18}H_{12}.$$

Similar additions with subsequent splitting-up appear to occur with many other non-saturated components of the products of tar distillations, possibly also with compounds containing O and S, and it may be assumed that the pitch consists essentially of substances formed in this manner, of very high boiling-point.

General Properties; Hard and Soft Pitch.

We have seen in the preceding chapter that the distillation of coal-tar leaves a more or less consistent residue, according to the way in which it has been conducted. If only the light oil is distilled off (that is, if the process ceases when the specific gravity of the distillate equals that of water), the residue in the retort (about 80 per cent. of the weight of the tar) is sometimes called *asphalt* (*brai liquide*). It is very unusual now to carry on the process in this way; what is called "asphalt" by tar-distillers is made by mixing ordinary pitch with a suitable quantity of creosote oil, and most commonly it is soft pitch mixed with sand, etc. (*vide infra*).

If about 10 per cent. more is distilled off, the residue is *soft pitch;* next comes moderately hard pitch; and *hard pitch* is obtained if the process is carried on as far as wrought-iron vessels will permit (p. 371). Another rule is this: *Soft pitch* is obtained if the distillation is interrupted before driving off the anthracene, when the specific gravity of the distilling oils is about 1·090; *hard pitch*, if it is continued till the oils show sp. gr. 1·120; moderately hard pitch, if the distillation is interrupted between these two stages.[1]

The "asphalt," if obtained by merely distilling off the light oils, naturally contains all the constituents of creosote oil (that is, naphthalene, phenols, etc.), together with all higher-boiling substances. Proper "pitch" always contains the least volatile components of coal-tar, such as anthracene, phenanthrene, chrysene, pyrene, etc., together with several ill-defined substances, as bitumen, etc., and free carbon, or rather coal-dust or coke-dust in an extremely fine state of division. It is, however, possible that something nearly approaching real carbon, or graphite, formed by the decomposition of tar-oils on the hot sides of the retorts, is also present in coal-tar. The value of coal-tar is greatly diminished if there is a considerable quantity of such "free carbon" present, which always comprises coal-dust or coke-dust as well (cf. *supra*, pp. 321 and 426, and *infra*, p. 469).

Behrens,[2] by successively digesting hard pitch, freed from all oils up to sp. gr. 1·120, with cold benzene, carbon bisulphide, boiling benzene, and boiling alcohol, obtained 23·54 per cent. of a black powder, containing 90·836 C, 3·058 H, and 0·398 ash; when treated somewhat differently, the residue yielded 91·921 C, 3·157 H, and 0·872 ash, quite similar to South Welsh anthracite (*cf.* the patent of E. Heusser, further on).

According to Habets,[3] good hard pitch consists of 75·32 per cent. C, 8·19 H, 16·06 O, 0·43 ash, and its sp. gr. is 1·275 to 1·286.

Donath and Asriel,[4] in examining soft pitch, moderately

[1] The manufacture of a pitch from coal-tar without distillation, by a treatment with sulphuric acid, has been mentioned, *supra*, pp. 291 *et seq.*

[2] *Dingl. polyt. J.*, ccviii., 369.

[3] Guelt, *Steinkohlenbriquettes*, p. 23.

[4] *Chem. Centr.*, 1903, i., 1099.

hard pitch, and hard pitch from the same factory, obtained with it the following results per cent. :—

	C.	H.	N.	S.	Extract with petroleum spirit.	Extract with benzene.	Extract with CS_2.	Residue.
Soft pitch . .	91·8	4·62	?	?	25·05	44·98	6·57	22·82
Intermediate pitch	94·32	3·98	0·148	0·77	15·14	40·03	7·10	38·16
Hard pitch . .	93·16	4·36	?	?	15·51	39·46	15·21	29·39

Hard pitch, on being extracted with petroleum spirit of 56° to 60° boiling-point, yielded a very tough, viscous residue, containing 2·19 per cent. anthracene. The extractions with benzene and that with CS_2 followed in rotation. The last residue was a non-lustrous, deep black powder, containing 89·2 C, 2·3 H, 0·7 N, 7·13 O, 0·67 ashes (O calculated from difference). The constituent which imparts the black colour to pitch is comparatively the richest in oxygen. Part of this residue is undoubtedly more or less unchanged coal-dust.

Hard pitch is easily divided into flakes or lumps, which do not soften even in the sun, and can be always sent out in bulk, whether in railway-trucks or in ships, at all seasons of the year. Moderately hard pitch can be sent out in bulk in railway-trucks, but not in ships, where it would coalesce into a mass, at least in the warm season. Hence the English tar-distillers mostly make moderately hard pitch; and so do the French, at least in summer. Soft pitch can only be sent out in casks, and is mostly run into these direct from the tar-stills. According to the Alkali Inspector's Report for 1893, p. 114, 95 per cent. of the pitch made in England is sold in the medium-hard stage, after distilling up to hard pitch and softening it with creosote oil; only 1 or 2 per cent. is sold in the state of hard pitch, and 3 or 4 per cent. as soft pitch.

The manufacturers of patent fuel, especially in Belgium, greatly prefer soft pitch to hard; hence the German tar-distillers are compelled to make at most only moderately hard pitch. During the winter months much soft pitch is sent out to those works which require in summer a moderately hard or even decidedly hard pitch.

When it is not possible to soften the pitch while it remains

liquid in the still, or else in the pitch-cooler, by pumping in oils, the operation is more complicated. This occurs when hard pitch has to be softened by the buyer to make it more suitable for the manufacture of patent fuel. For this purpose special *pitch-revivifying apparatus* have been constructed. Such an apparatus, as employed at the Blanzy coal-mines, is described in Payen's *Précis de Chimie industrielle*, 1878, ii., p. 919, as follows:—In Fig. 126, C is an upright boiler, 6 ft. in diameter, 9 ft. 2 ins. high, holding about 320 cub. ft., and provided with a steam-jacket. In the centre revolves an endless screw, V, surrounded by an annular casing, which is heated by steam entering at *f* and issuing at *h* into the outer jacket; the condensation-water is discharged by *r*. At the bottom are the annular gratings G G (made of perforated iron plate) for retaining large pieces, the pipe S for discharging the revivified pitch, and a cleaning-hole (*t*). The boiler C is surmounted by a wrought-iron chamber, D, of equal size, to receive the froth formed during the operation. Here is a manhole, T, and a gland for the passage of the screw, V. The work is carried on in this way:—A certain quantity of tar, creosote oil, or the like, is let into the apparatus through the pipe *k*; steam is admitted till the heat rises to 150°; the screw is made to revolve; and the pitch which is to be revivified is gradually charged through the manhole T. More tar and pitch are added till the boiler contains about 9 tons of materials. The plate P prevents the pitch thrown in at T from falling upon the screw. The pitch is soon melted in the hot tar; the mixture passes through the sieve G, is lifted by the screw V, and thrown out again on the top. After eight hours all is melted and homogeneous; now the discharge-cock is opened and the revivified pitch run into coolers, after which the operation can be commenced anew.

The revivification can be effected by means of creosote oil, naphthalene, or tar which is merely deprived of the light oil (=asphalt). It has been found at Blanzy that the creosote oil does not modify the agglomerating property of pitch, but merely renders it more liquid; naphthalene increases the agglomerating property, but causes solidification at too low a temperature; the best of all is tar deprived of light oils, of which 10 or 20 parts are taken for 100 of pitch. [Prob-

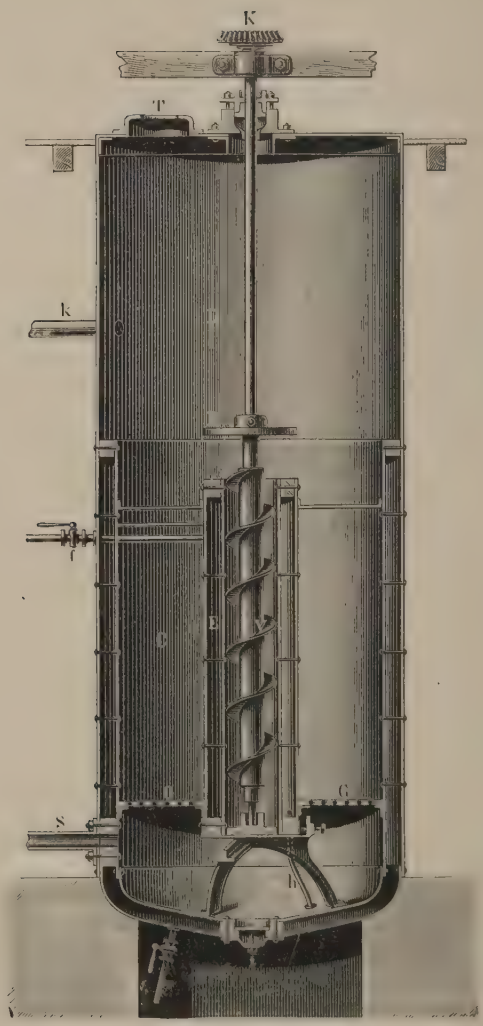


FIG. 126.

ably the last tar-oils, deprived of anthracene, would be still better.]

W. J. and A. Malden (B.P. 12230, of 1907; Fr. P. 387674) state that they improve the tenacity and raise the softening point of (tar and) pitch by the following treatment. They liquefy the material first moderately so as to prevent the evaporation of oils, say to 50° or 60°, add to it 10 per cent. of manganese peroxide, with which the liquid substance is well mixed, then 5 per cent. of sulphuric acid of sp. gr. 1·84, and heat up to about 180° C. At this point the temperature is maintained, until the evaporation is equal to about ¼ per cent. in the last 15 minutes of the treatment, whereupon the mass is allowed to cool. By this treatment the softening point is raised to such an extent that the disadvantages arising in the use of briquettes made in the ordinary way do not occur.

The Manufacture of Patent fuel (*Briquettes*).

The principal employment of coal-tar pitch is for making *patent fuel* (*briquettes*) from small coal or coke-breeze. A detailed description of this industry does not come within the scope of this work; a number of special treatises have been written upon it, as the French one by G. Franquoy (1860) and the German ones by Gurlt (*Die Bereitung der Steinkohlen-briquettes*, Braunschweig, 1880), by Jünemann (*Die Briquette-industrie*, Hartleben's Verlag), and by Preissig (*Die Presskohlen Industrie*, Freiberg, 1887); and the technical cyclopædias also contain much information upon this subject, of which we shall only give the outlines here.

This industry would appear to be due to Ferrand and Marsais, who in 1832 obtained a French patent for employing coal-tar for this purpose. Marsais after 1842 employed soft pitch, and in the same year founded the works at Bérard, near St Etienne. Hard pitch was used in 1843 in England by Wylam, and since 1854 in France. The patent fuel made near St Etienne was sold by the name of "péras."

The manufacture of patent fuel is the most natural outlet for the immense quantities of small coal (slack, duff, etc.)

obtained at the majority of coal-pits, and saleable only at a very low price or sometimes not at all. It is remarkable that this industry has been principally developed in France and Belgium, but comparatively less in England and Germany, although there are enormous quantities of raw material available, for instance in Westphalia. The production of patent fuel per annum was estimated as follows for the year 1897: In France, 1·2 or 1·5 millions of tons (50 or 60 works), mostly for steamships and railway engines; Belgium, 1 million tons (about 20 works); Netherlands, 1 works; England and Scotland, 1 million tons (800,000 tons being exported); Germany, about 1 million tons. There are also factories in Austria, Russia, Spain, America, etc.

For Germany we can quote only the production of the chief district, that of Rhineland—Westphalia, as shown by the Dortmund producer's union.

Year.	Briquettes produced.	Average price per ton.	Pitch consumed.	Average price of pitch at works.
	Tons.	Mark.	Tons.	Mark.
1894	754,414	8·82	60,785	43·75
1895	796,363	9·07	59,032	45·50
1896	830,980	9·34	65,067	43·00
1897	943,732	9·99	70,631	35·35
1898	1,078,338	10·22	79,757	30·75
1899	1,295,113	10·66	103,485	34·00
1900	1,530,816	12·27	108,976	42·50
1901	1,563,928	13·33	116,956	43·00
1902	1,610,215	11·20	112,795	42·00
1903	1,780,390	11·47	113,923	54·50

According to Bock (*Z. angew. Chem.*, 1908, p. 2520), that district in 1907 produced 2,800,000 tons of patent fuel.

The selling price of briquettes is usually the same as that of lump coal, sometimes higher. They are mostly made in prismatic forms, sometimes in the shape of cylinders, balls, or the like, and especially of perforated bricks. The weight of each brick is from 33 lb down to 1½ ounces. The specific weight ranges from 1·10 to 1·40.

Good briquettes ought not to weigh above 22 lb., and should

possess the crushing strain of natural coals. For this purpose they must contain at least 5 per cent. of pitch if very strongly pressed, or 7 to 8 per cent. if made with less pressure. They must not leave more than from 6·5 to 6·75 per cent. of ash if intended for locomotive use, or 10 per cent. if for steamboat use. Their regular parallelopiped shape permits easy stowage in the bunkers. The loss in transit by disintegration is only 1 or 2 per cent., against 30 to 50 per cent. in the case of coals. They ought not to fall to pieces in the fire. Good patent fuel has 10 per cent. more heating-power than good steam-coal; it makes much less dirt, and if manufactured with hard pitch, less black smoke than most descriptions of coal. One very important advantage of patent fuel is, that the fireman knows exactly how many pieces he has to put into the furnace at certain intervals in order to produce a certain effect, and that the foreman or manager can estimate whether this has been done by a single glance at the briquettes stacked beside the furnace.

Briquettes are mostly made with moderately soft pitch, but it should not be too soft. Briquettes made with hard pitch give less black smoke than the coal they are made of, according to experiments made at the German Imperial Wharf at Wilhelmshaven between 1874 and 1886. If hard pitch is to be used for this purpose, it must be ground and the mixture brought to a higher temperature; the injurious action upon the eyes of the workmen is a great drawback in this case.

Non-bituminous coal naturally requires a greater addition of pitch than bituminous coal.

The following notes on the development of this industry are mainly based on a prize essay by Berg.[1] The coal to be used ought not to contain more than a limited quantity of ashes, and should possess a certain amount of resistance against crushing in transit. Of the different processes, that of Baroulier (adding to coal-dust some bituminous caking-coal, pressing and heating in separate vessels) has not been successful, being too expensive and not yielding a product capable of bearing a long transit. Not much more successful have been a number of agglomerating substances successively proposed, such as vegetable and animal fats and oils, soap, gelatinous

[1] *Zeit. für Berg-, Hütten- und Salinenwesen*, 1880, p. 148.

substances (glue, etc.), mucilaginous decoctions of roots or whole plants, rosins, magnesia cement, Carragheen moss, and wood-pulp. The only substances in general use are coal-tar and soft and hard pitch. Soft pitch, mostly used in France, is melted in suitable pans, and mixed with the coals in the liquid state: hard pitch, mostly used in Belgium,[1] is mixed with the coal in the state of powder, and the mixture softened by means of steam superheated to 300° ; or else it is heated by direct fire, either in a hearth provided with a horizontal agitator (Chauselle), or in a revolving circular hearth with vertical agitator (Biétrix). With this plan, 4½ per cent. of pitch is said to suffice. The coal is best if dressed, in order to free it from impurities, and then mixed with dry coal-dust to facilitate the pressing. Some presses have closed and others open moulds, the latter either with direct or indirect action. In Mazeline's direct-action press, the steam-cylinder, piston on rising forces, by means of a one-armed lever, the press-ram from below into the moulds, which are contained in a circular platform, revolving by means of a ratchet. The finished briquettes are forced out by the rams sliding along an inclined plane. The ratchet arrangement is liable to frequent breakage. In the indirectly acting machine of Middleton and Detowbay the pressure is caused by an angle-lever carried down by a weight ; the finished briquette is forced out by a second angle-lever. Here also the platform is turned round by a ratchet arrangement. In the similar machine of Hanrez, the lever presses at the same time from above and below, limited by a hydraulic ram ; the forcing-out is effected by an inclined plane, the revolution of the platform by a ratchet. In Durand and Marsais's machine (especially adapted for smaller work) the ram is pressed into the mould by an eccentric sheave, afterwards by a similar sheave the closing-plate is removed and the briquette pushed out. Another similar machine has been constructed by Biétrix.

In the case of machines with open moulds, the pressure is obtained by the friction of the mass at the conical mouth of the press. Hence they require more power than those just described,

[1] According to information received by me from other sources, it would appear that the opposite is the case, viz., that more hard pitch is used in France, more soft pitch in Belgium.

but do more work; they are as yet employed exclusively with soft pitch.[1]

In the most widely-used machine of this kind (Everard's) the tubular moulds are arranged radially in a circle, so that the eccentric attached to the vertical working shaft can by turns force the rams in and out of the moulds. At every back stroke of the ram a fresh mass is forced into the mould, which by the forward stroke is pressed against the old mass and forces this out of the open end of the mould. A similar machine, by Bouriez, permits the use of hard pitch also. Revollier's and Mazeline's machines are worked by hydraulic pressure.

Of recent patents for manufacturing patent fuel we will mention:—E. F. Treddar (Ger. P. 16017, of 1881); G. H. Lenk and W. H. Lehmann (Ger. P. 15789, 1881); G. J. P. Couffinhal (Ger. P. 15239, 1881); M. Neuhaus and O. Henniges (Ger. P. 18538, 1881); S. Butler (B. P. 7791, 1886). Bowing (Ger. P. 51099 and 58708) goes back to tar itself; also the Aktien-Gesellschaft für Theerprodukte (Ger. P. 63648), Jenker (Ger. P. 61166), and Bergmann (Ger. P. 101299). G. S. & C. Cory (B. P. 7772, 1884), mix 7 parts pitch with 1 part naphthalene.

Bornemisza & Kopal (Ger. P. 31644) made a kind of artificial fuel by mixing 100 parts of melted coal-tar pitch with wood-cuttings or other vegetable refuse, allowing to cool down on stone slabs, moulding into pieces 4 × 2 ins., with a central hole, coking these pieces, putting on an iron rod, within a wire-gauge cylinder contained in an ordinary gas-retort, and pressing the product once more while still hot. Huttemann & Spieker (Ger. P. 86827) make briquettes with a mixture of 3 or 4 per cent. pitch and 1 per cent. rosin.

Schnauder & Bergmann (Ger. P. 101299) mix finely ground coal or coke with two or three times its weight of melted pitch. This mixture, moulded into blocks, is to be used like ordinary pitch in the manufacture of briquettes; it is asserted that it possesses the same binding powers, and does not so easily soften in warm weather.

[1] The latter process is exactly analogous to that of moulding bricks—the machines that work for dry clay being constructed with closed moulds, those for wet clay with conical mouthpieces (dies). But it is well known that the former take much more power and have a much larger output than the latter. Is the opposite really the case with patent-fuel presses?

Conring (Ger. P. 108197) makes briquettes by heating 1870 parts ground coal to 150°, 80 parts pitch to 160°, intimately mixing them together, adding milk of lime made from 50 parts lime, and working it all up in a press.

Schöndeling (*Z. angew. Chem.*, 1906, 348) reports on the employment of Bohemian lignite for the manufacture of briquettes.

Plate & Lieb (Ger. P. 164291) prescribe the use of *wet* coal (not below 10 per cent. water) and subsequent heating of the briquettes to 100° C., which causes the pitch to be very finely divided by the steam, and therefore permits reducing the amount of pitch to only 3 per cent.

Pauline Grayson has obtained a German patent (No. 163367) for a very remarkable mixture: 6 per cent. gypsum, 16 lime or cement, 20 water, 12 mineral oil, 6 pitch or rosin, which leaves only 32 per cent. for coal!

H. S. Robertson (B. P. 20281, 1906) for the manufacture of artifical fuel, mixes a tarry substance with hydrocarbon oil, removes the precipitated solid matter, and employs the fluid as a solvent for resinous matter, with or without the addition of tar and common salt.

Schmetz & Schramm (Ger. P. 141344) make briquettes with a smaller percentage of pitch than is otherwise required, by melting hard pitch with 60 per cent. of coal powder, passed through a sieve with from 50 to 250 meshes per superficial centimetre. Of such coal, up to 60 per cent. can be incorporated with the pitch.

Testing the Quality of Briquettes.

The tests usually made at the patent-fuel works is very uncertain. The makers try the *hot* briquettes, as they come from the press, for their resistance by hand, or by dropping them from a height of 6 or 9 ft. on to a stone floor. This is very deceptive; briquettes made with pitch of 50° or 55° softening point thus seem to be less resistant at 75° than those made with harder pitch (70° to 75° softening point); but in the *cold* the former are really harder than the latter. That test is also influenced by the amount of pressure and the violence of the blow.

Le Ray (*Chem. Centr.*, 1900, ii., 1298) estimates the quantity of pitch contained in the briquettes (which should be about 8 per

cent.) by grinding up a sample with five to ten times its weight of coarse sand, and treating in a Soxhlet extractor with a mixture of equal parts of petroleum spirit and bisulphide of carbon.

J. E. Mills (*Oil, Paint, and Drug Reporter*, 1908, 17th to 27th July; *J. Soc. Chem. Ind.*, 1908, p. 887) describes the experiments carried out at the United States Government fuel testing at St Louis for determining the relative values of the various binding agents for briquettes, among which, of course, tars and pitches from coal hold a prominent place.

The testing of the pitch intended for making briquettes will be described at the close of this chapter.

Varnishes made with Pitch; Refined (prepared) Tar.

A very rational employment of coal-tar pitch is for making varnishes, for iron especially, but also for wood, etc.—of course all of them black. They are made in a very simple way, by melting pitch with various products of tar-distillation, and hence require no admixture of any foreign matter. No plant is necessary but an open pan set in a covered place, so as to be heated from without; but it is certainly preferable to employ a closed pan with a mechanical agitator. The melting-pan may be made either of cast- or wrought-iron; but it is best if made of the latter, because then no cracking (very dangerous in this case!) can occur. It may be an upright cylinder with convex bottom, or a horizontal boiler. For working on a large scale, a mixing-apparatus like that represented in Fig. 126, p. 434, is preferable.

In this pan the whole quantity of pitch to be worked up is melted along with a little of the oil to be employed, which promotes the melting of the pitch and prevents its speedy solidification. Still the temperature will rise pretty high before all the pitch is melted, and it is best to let it cool down a little, lest the oils now added should be raised to the boiling-point, which will, of course, most readily happen with light oil or naphtha. But the cooling must never be allowed to go so far that some part of the mass begins to solidify. Now the remainder of the oil is added very gradually, stirring each portion completely into the mass. From time to time a sample

is taken out and cooled, to see whether the proper consistency has been attained.

The commonest kind of varnish is made in the manner just described, from pitch and creosote oil. In this case even a simpler process may be followed. The tar is distilled (if need be, in a separate small still) till the light oil has passed and heavy oil begins to pass, or till all the "middle oil" has passed over, say up to 240°. The fire is now drawn out, the still allowed to cool down a little, and the residue ("asphalt") diluted within the still itself with the necessary quantity of creosote oil, say ¾ of the weight of the pitch, after which it is run off in the liquid state. Or else the distillation is carried on to hard pitch, in order to obtain the anthracene; the heavy oil, freed from anthracene and, if possible, from naphthalene, is run in till the necessary degree of thinness is attained; and the mass is well mixed. We have described this process above, pp. 369 and 383, as it is carried out within the stills themselves; but sometimes the creosote oil is mixed with the hard pitch in the pitch-cooler, a pipe conducting it from a store tank into the fluid pitch within the cooler. The varnish thus obtained, in England called *refined tar*, in Germany known as *prepared tar* or *artificial Stockholm tar*, is less valuable to the tar-distiller than raw tar, since the more valuable components—benzol, phenol, anthracene, and partly naphthalene—have been removed; on the other hand, it is much more valuable than raw tar for many purposes—as a paint, for the manufacture of roofing-felt, for roperies, etc. It penetrates much more quickly and deeply into wood, stone, etc., than raw or even boiled coal-tar, and dries much more quickly, even more so than wood-tar (real Stockholm tar). For making dust-free roads it is also much better than raw tar, *cf.* pp. 288 *et seq.* It is greatly to be recommended for alkali and other chemical works, for painting any wood-, iron-, or stone-work needing protection against acids, chlorine, etc. Such prepared tar is especially very much to be preferred to boiled tar for painting iron (where raw tar, owing to its ammonia, is quite inadmissible), as it dries both much more quickly and without leaving cracks, and forms a good, shining coat. The drying takes from twelve to twenty-four hours, according to the weather. As this sort of varnish forms a pretty thick coat, it is only applicable to coarse ironwork, but is excellent for this.

Most of the "refined tar" is used in the manufacture of roofing-felt, a great deal also for the manufacture of the basic lining of the converters in the Thomas-Gilchrist steel-making process.

Disputes concerning the quality of "refined tar" have made it desirable to possess *methods for testing the quality* of that substance in a proper manner. Such methods have been worked out by myself,[1] and have been found to be very useful in practice. They comprise the following operations:—

1. Estimation of *specific gravity*, as described p. 426.

2. Estimation of *viscosity*.—The ordinary instruments for this purpose, based on measuring the velocity of issue from a small orifice, cannot be employed in this case, as the apparatus would be too difficult to clean. The instrument described below, based on the velocity of immersion, obviates this difficulty and, although not scientifically accurate, is altogether sufficiently so for practical purposes.

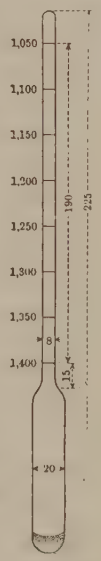


FIG. 127.

Lunge's "tar-tester," as shown in Fig. 127, somewhat resembles a hydrometer, but is made of very strong glass, in order to allow its being easily cleaned. For the same reason, but chiefly for the purpose of a more uniform velocity of immersion, the lower part is made without the ordinary contraction and bulb, of cylindrical shape with a semicircular end. The following dimensions have been found to answer the purpose:—Length of lower parts, inclusive of the upper and lower ends, 100 mm., outside diameter 20 mm. Length of upper part 225 mm., outside diameter 8 mm. Beginning of scale 15 mm. above the conical end of the lower part. Length of scale 190 mm. The lower point of the scale marks the specific gravity 1·400, the top of the scale 1·050. The point 1·250 is 81 to 83 mm. above the end of the conical portion. Weight 39 g., with a margin of ±0·5 grm.

The manipulation of the tar-tester is as follows:—The tar is

[1] Lunge, *Z. angew. Chem.*, 1894, p. 449.

poured into a glass cylinder which, after immersion of the tester, must be as nearly as possible full, to facilitate the observations. The tar is stirred with a wire bent at the bottom into a ring, and its temperature determined to 0°·5 C. The observations should be made at 15° C., and the cylinder must be brought to this temperature by placing it in a water-bath, with frequent stirring. The tar-tester is now suspended above the cylinder, preferably by means of a spring-clamp. It is immersed exactly to point 1·250, taken out and allowed to drain for three minutes, suspended as above. Only then the proper observations begin. A seconds-watch is taken in one hand, the tester in the other, so that its bottom just touches the surface of the tar, and when a full minute is reached the tester is allowed to drop. It will at first fall very quickly, until the wider part is reached, afterwards but slowly. If it assumes a slanting position and touches the side of the cylinder, it must be righted by a gentle push. Directly the point 1·250 has been reached, the number of seconds is read on the watch, the tester is taken out and is allowed to drain for two or three minutes before making the next observation. Three or four, or even more, tests must be made, and they should not differ more than two or three seconds.

Of course the specific gravity of the tar can be taken by means of the same instrument; but for estimating the viscosity the point 1·250 should be observed, because the last sinking takes place much too slowly.

3. Estimation of the *volatile constituents*.—This cannot very well be performed by an ordinary distillation. The following method seems rather more complicated, but is decidedly preferable, as it yields uniform results. One hundred grams of the tar is distilled from a tubulated retort of refractory glass, protected by asbestos paper, until a certain quantity of liquid has passed over into a graduated cylinder. The specific gravity of this distillate is ascertained, as well as that of the pitch remaining in the retort (after allowing this to cool and breaking it) and the softening point of the latter, as described later on. If the first experiment does not yield proper pitch of medium hardness, a second and, in case of need, a third experiment, with more or less distillate, must be made.

In buying and selling refined tar, distinct conditions should be stated for the specific gravity, viscosity, and minimum

quantity of distillate. The last and most troublesome test can usually be omitted, as the two former will suffice for most purposes. We cannot here quote special figures, since for various purposes different conditions will be required.

A better kind of varnish is obtained by melting pitch with light oil in the above-described manner. For this purpose not the light oil distilled from the tar, but the last fraction from the light-oil still, or the oil taken away from the carbolate of soda (*cf.* Chapter IX.), is employed, which is deprived of its more valuable components. For 100 parts of moderately hard pitch about 60 parts of light oil may be calculated. This varnish gives a more lustrous and smooth surface than the former, and leaves a much thinner coat. Its drying-time varies from four to six hours ; and it can be employed for finer ironwork.

Lastly, more quickly-drying and thinner varnishes can be obtained in all gradations, by substituting naphtha for part of the light oil, either the commonest burning-naphtha being employed or else some made on purpose by carrying on the rectification of benzol by steam beyond the usual termination. The rule is, first to work up all the light oil with the pitch, and then to add the naphtha, keeping the mixture as hot as is consistent with the volatility of the naphtha. Besides, very thorough and long-continued stirring is necessary, since naphtha is not so easily incorporated with the varnish as the heavier oils, and the varnish would otherwise be very likely to separate into a black deposit with naphtha floating on the top. It is possible by means of very common naphtha to make varnishes that dry in an hour, or even in a quarter of an hour, which can be employed for any kind of hardware in which blackness is of no consequence.

All three kinds of varnish adhere firmly to iron, and after drying exhibit a considerable degree of hardness, together with glossy lustre and smoothness, and more of the latter in the case of the better descriptions.

A patent of Marchisis and Stevens (23rd Sept. 1870) seeks to improve such varnishes by heating with bleaching-powder or a solution of common salt and washing with copperas solution. Whether this does any good we cannot tell.

Chaumont[1] makes a varnish for wood and metals by dissolv-

[1] *Wagner's Jahresber.*, 1865, p. 686.

ing 300 parts of coal-tar asphalt in 100 carbon bisulphide. In lieu of such asphalt, natural bitumen or rosin may be employed. The materials are brought together in a closed vessel, to prevent the evaporation of the carbon bisulphide. In twelve to twenty-four hours the varnish (the smell of which will hardly recommend it) is ready for use.

Watson Smith (priv. comm.) recommends as a good varnish for tarpaulins one obtained by melting wood-tar pitch with the same weight of coal-tar creosote oil, freed as much as possible from naphthalene; also as a good metal-varnish one obtained by melting 6 lb. of dark rosin with a pint of boiled linseed oil and a gallon of creosote oil, to be mixed, for finer work, with a little gum and any kind of colouring-matter.

E. Heusser (Ger. P. 24231) extracts pitch with warm light tar-oil or benzoline. A solution is formed which, on evaporation, leaves a mass resembling native asphaltum. The residue left after extraction forms a black paint of great covering-power.

Roth (Ger. P. 152758) prepares a protecting compound from 33 parts heavy oil, 20 parts light oil, 47 parts pitch and aluminium oleate, which is sold by the name of "inertol" and is specially recommended for protecting iron and cement under water, such as in brick-tanks for drinking-water.

A German patent (86345) was obtained by the Aktien-Gesellschaft für Teer- und Erdöl-Industrie for an asphalt compound, to serve as a protection of wrought-iron water-pipes against corrosion. It is sold by the name "Cumanollack."

According to G. Kraemer (priv. comm.), a good varnish is obtained from oil-gas, tar-pitch (which contains but a few per cent. of free carbon), heavy benzol, and small quantities of crude carbolic acid.

Asphalt, Asphalt-paper, Roofing-felt, etc.

The term "asphalt" was formerly restricted to what is now called "natural asphalt" or "bitumen," of which in 1901 the United States produced 63,134 short tons, and Sicily exported in the same year 62,770 tons. This substance is principally used for street-paving in various forms, and cannot for this purpose be entirely replaced by the product from coal-tar, to which the name of "asphalt" is also given. A very instructive series of

papers on natural asphalt is found in the *Chem. Trade J.*, 1902, xxxi., pp. 184, 207, 228, 252; and in *Baumaterialienkunde*, 1906, xi., p. 12 (by Malenkovic). In this book, of course, we use the word "asphalt" as denoting a product obtained from coal-tar.

Marcusson and Eickmann, in the *Chem. Zeit.*, 1908, No. 80, discuss the processes for distinguishing natural asphalt from the products made from tar, petroleum, etc.; these always contain paraffin, which is absent in natural asphalt.

Professor Holde demands that the expression "asphalt" should be restricted to such natural asphalts which are almost entirely soluble in benzol and contain from 1·5 to 10 per cent. of sulphur, as employed for building purposes, for preserving materials against humidity, for making varnishes, etc. Materials obtained artificially in the distillation of coal-tar, petroleum, etc., and used as surrogate for natural asphalt, ought always to be denoted in such manner that no confusion with natural asphalt can take place.

Asphalt, both that obtained directly in the distillation of coal-tar and that made by mixing pitch with heavy oils and with solid substances, is useful for many purposes. It is employed for keeping the subsoil moisture from metal pipes, iron tanks, etc., sunk in the ground. For this purpose the semi-liquid mass is mixed with sand, ashes, etc., into a lumpy paste, of which a thickness of 4 or 6 ins. is employed. We shall quote particulars of such mixtures below.

Such asphalt, made direct from tar, is not so frequently used now as formerly; but similar mixtures are artificially made, by driving off all the creosote and anthracene oil, and pumping back the heavy oils, meanwhile freed from their more valuable components, as phenol and anthracene, till the desired consistency of the residue has been attained. In this way is obtained not merely soft pitch, but also asphalt, and, with greater dilution, even "refined tar" (p. 442) or "artificial Stockholm tar," which is largely employed in the manufacture of roofing-felt (see below).

The employment of pitch or asphalt for *street-paving* is to be recommended in many respects. When used as a cement for joining the paving-stones, it makes the ground impermeable to the impurities from below and does not permit the passage of noxious effluvia. Tar-pitch is also used as a direct *substitute*

for natural asphalt, but only in combination with the latter, for asphalting footpaths and for insulating foundation-walls from the ground-moisture. The mixture is melted in pans in the usual way; sand, brick-dust, ashes, chalk, and the like are added till the mass has become thick enough (for which purpose about four times the weight of the pitch will be necessary); the whole is well mixed, preferably by grinding in a pug-mill, and used hot. For footpaths the pitch is ground up with an equal weight of sandy or stony material, melted in a pan, and, before being laid down, is mixed with an equal quantity of gravel; so that the finished pavement contains about 30 per cent. of pitch. But it is not advisable to employ coal-tar pitch alone, without any natural bitumen; the latter is much more intimately combined with the earthy matters than the former can be. A mixture of the two is very suitable, and is cheaper than natural asphalt alone. In a similar way, moulded blocks are made from pitch and ground rock.

At some Scotch tar-works the pitch is run directly from the tar-still into a pug-mill, where it is intimately mixed with sand, sometimes also with chalk. From this mill the mixture, while still liquid, is run off into sand moulds to solidify. During the whole process, until the completed asphalt becomes cool, offensive vapours are given off; the pug-mill or mixing-pan ought therefore to be covered with a hood, and the vapours carried away into a chimney-stack by means of a pipe. The space between the edge of the hood and the mill or pan should be enclosed by sacking which can be opened at certain places as requisite for manipulation. (Dr Ballard.)

Gobin (B. P. 1865, 9th May 1878) melts 15 parts of bituminous shale with 35 parts of coal-tar pitch in a pan, till the froth which at first arises has subsided. Then he adds 10 parts of coke and 130 of limestone, both crushed, well mixed, and dehydrated by heating above 100°. Before cooling, he adds another 160 parts of gravel, well dried by heat. For street-pavements he increases the quantity of gravel up to 190 parts, moulds the mass into blocks of about $8 \times 6 \times 4$ ins., and lays these, like ordinary paving-stones, on a bed of gravel or sand.

Daguzan (Ger. P. 4999) mixes tar, first completely dehydrated by heat (probably he means "asphalt"), with previously "calcined," finely ground limestone or marble (quicklime?), 5

per cent. oxide of iron, potassium silicate, calcium sulphate, etc.

E. G. Williams (B. P. 13595, 1890) prepares asphalt-resisting acids and oils by mixing sand with pitch, freed from creosote oil.

Hannemann & Boisly (Ger. P. 83550) heat coal-tar pitch with sulphur, and treat the melted mixture with bleaching-powder; after cooling, the mass is ground, mixed with some thickening stuff and heated again.

G. F. Sidney (B. P. 15316, 1896) heats tar or pitch during two to four hours to 350°, till the sp. gr. 1·261 has been reached, and then mixes it with ground schist or ashes.

Dörr (Hung. P., 28th June 1899) manufactures a new preparation from coal-tar pitch by mixing the fresh tar with solid substances of an organic or inorganic kind, and heating the mixture until it has acquired by evaporation and pressure the required consistency, ranging from the hardness of hard wood to that of stone. By this process a comparatively small amount of the cementing substance is required, and the result is a uniform, hard mass, without any of the disagreeable properties of asphalt.

The best *tar pavement*, according to communications from Mr. S. B. Boulton, is made with refined tar (p. 442), or at least with thin tar-asphalt, in this way:—There is first a thin layer of concrete made, upon which is spread a mixture of tar with washed gravel free from loam. The gravel is thrown into a pan filled with hot tar; when thoroughly soaked, it is spread on the concrete and rammed down. After cooling, a top layer is formed, made of dry sand, hot tar, and a little pitch, in order to fill up the interstices between the gravel and produce a smooth surface. According to H. Riley,[1] macadamized roads are made in England as follows:—The material consists of slags and cinders from blast-furnaces and iron-mills, Yorkshire sandstone Derbyshire limestone, and Leicestershire granite. It is crushed like road-metal and dried in furnaces or ovens. The tarry mixture varies in different localities. Some employ gas-tar and pitch, boiled together; others prefer a mixture of tar and creosote oil. The proportions differ according to the quality of the tar.

[1] Quoted by Jahn, *Zeitsch. f. Transpertwesen*, 1898, p. 329.

At Gainsborough the proportions employed are to each ton of ballast 13 galls. of tar and 26 lb. of pitch. The ballast dried on hot plates, is put into conical heaps, the tarry mixture is poured on and is worked through until each stone is throughly covered. It is preferable to leave the mixture lying for a month or two, covered up, to give time for the tar to soak into the porous stones. A 4-inch layer of this is placed on the foundation and rolled down by a steam-roller; and a covering layer, 1 in. thick, is made of hard material, broken quite small and treated exactly like the former. At last the whole surface is sprinkled with limestone- or cinder-dust, and the street is blocked against traffic for about a week. This work should not be done during the winter months; the warmer the weather the more durable is this pavement, which costs about 8s. 6d. per ton, and which is extensively used in Great Britain.

Thenius[1] proposes mixing soft pitch with 10 per cent. of rosin oil, which is to make it more like natural asphalt, or with 50 to 60 per cent. of crushed limestone. This mixture is moulded into blocks, and is, with the addition of 25 per cent. of ground gravel or basalt, cast into mosaic plates for pavements tables, etc.

Tar-asphalt can be considerably improved by the addition of *brimstone*. A. Winkler[2] adds to coal-tar asphalt (in the sense of the term adopted in this chapter) 5 per cent. of brimstone in small quantities, heating the mixture every time till no more sulphuretted hydrogen is given off. Probably, in the heating, the sulphur decomposes the components rich in hydrogen, and thus renders the residue less fusible. Thus 75 per cent. of the tar is obtained as good asphalt, which does not soften in boiling water. A further proposal of his does not seem practicable, viz., to add 20 per cent. of brimstone to the tar before distillation; it is said that in this case only water and sulphuretted hydrogen escape during the heating, and good asphalt is obtained, equal in weight to the tar employed. The expense, the action of the sulphur on the metal of the stills, and the nuisance caused by the sulphuretted hydrogen, would be objections.

A similar mixture is *Häusler's wood-cement*, well known in

[1] *Technische Verwendung des Steinkohlentheers*, p. 117 *et seq.*

[2] *Chem. Centr.*, 1858, p. 337.

Germany as a roof-covering. This kind of roof is very much employed in Germany and Switzerland, being practically fireproof, a bad conductor of heat, and almost indestructible. This cement is made of 60 parts dehydrated coal-tar, 15 pitch, and 25 brimstone. The mass should be kept from superheating, and the fumes discharged into the open air or under a hood, where the sulphuretted hydrogen, going off in great quantity, cannot injure the workmen.

G. Friedrich & Co. (Ger. P. 61555) assert that a mixture of various tars with pitch, rosin, brimstone, molasses, solution of indiarubber, etc., furnishes a wood-cement workable in the cold. Other modifications are Felten's "vegetable asphalt" and Rusch's "chlorite-cement"; but they do not appear to be real improvements on the original.

Petersen-Kinberg, in his above-quoted book, p. 203, prescribes running 1500 litres of "refined tar" (p. 442) from the tar-still at a temperature of 270° C. into a mixing vessel and quite gradually adding 6 litres of melted brimstone, continuing the agitation until all froth has disappeared.

Coal-tar asphalt, or very soft pitch, is also employed for manufacturing *asphalt pipes*. This industry, introduced by Jalourean, has been minutely described by Behrens.[1] Endless hemp paper, 7 ft. wide, is passed through a semicylindrical pan set in a furnace and filled with hot pitch.[2] A roller revolving in the pan takes up the paper soaked with pitch and conveys it to a smaller roller, forming the core of the pipe, round which about 100 layers of paper are wound. When the proper thickness has been obtained, fine sand is dusted on, and the whole is exposed to considerable pressure, which increases the compactness and homogeneity of the mass. After a short cooling in water, the core (which should previously be rubbed with soft soap (is drawn out by means of a crane, and the pipe is once more cooled by water. The joints of the pipes are made by iron flanges fixed upon them, or by thimbles formed of a wider piece of asphalt piping, and fastened on the pipe by a mixture of pitch and brimstone, or else by winding round

[1] *Dingl. polyt. J.*, ccviii., p. 377.

[2] That Behrens does not mean real pitch, but either asphalt or very soft pitch, is apparent from the fact that paper would be partially destroyed at the melting temperature of hard pitch.

them ten or twelve folds of linen cloth soaked in melted pitch. Similarly, any necessary elbow-pieces and bends are made, often at the place where the pipes are laid down.

According to the nature of the pitch employed, the pipes have different qualities, which must be taken into account in using them. If made with very soft, oily pitch, the pipes offer great resistance to the penetration of water, and hence are excellent for water-pipes in marshy ground. Those made of harder pitch offer a greater resistance to distortion by a higher temperature. Of course asphalt pipes can only be employed for conveying cold liquids or gases; but, with this restriction, they can be used for many purposes, both on account of their relatively low price and their valuable qualities. They resist a pressure of 33 atmospheres from within [?], and are sufficiently elastic for their joints not to break in case the ground settles down; they are not subject to be frozen up, being bad conductors of heat; they are not acted upon by dilute acids or alkalis, and can be laid in any soil. They are chiefly employed for conveying water, acids, air-blasts, for pit-ventilation, for covering underground telegraph-wires, for speaking-tubes, and sometimes for gas-pipes.

Such asphalt pipes and semicircular spouts made by cutting them in halves are excellent for carrying away waste liquors of an acid nature in chemical laboratories, and even in chemical factories, so long as they are not exposed to any heat.

Pipes of another kind are made from (probably harder) pitch by mixing it with gravel and casting it in moulds over a core of thin sheet-iron; the outside is covered with gravel, which is pressed or rolled in while the mass is still warm. The walls of these tubes must be very thick, as they are brittle. These pipes, manufactured by Chameroy, are extensively employed in Paris as water-pipes.

Doehring (Ger. P. No. 36666, 1885) has described a process for manufacturing pipes with a *glass core* and a jacket of paper, wood-cement, or soft pitch. Such pipes are resistant against liquids inside, and much more durable than glass tubes. They are made by the apparatus shown in Fig. 128, containing a winding-roller A and the wood-cement reservoir B, which is provided with a steam-pipe.

When using any kind of asphalt tubes, it must never be forgotten that they are liable to be distorted by heat.

Behrens (*loc. cit.*) also describes the manufacture of *asphalt-paper* as a substitute for wax-paper. Ordinary wrapping-paper is wound off from a roller upon a heated drum, upon which a scraper is fixed. Melted pitch runs down in front of this to a depth of $1\frac{1}{2}$ in. The paper thus covered with a thin film of asphalt runs over several rollers, and is ultimately wound round the last. Another kind of paper, consisting of a thin layer of pitch between two layers of paper, which is much used for covering damp walls, is made in a similar manner.

Another use of soft coal-tar pitch is for *insulating subterraneous*

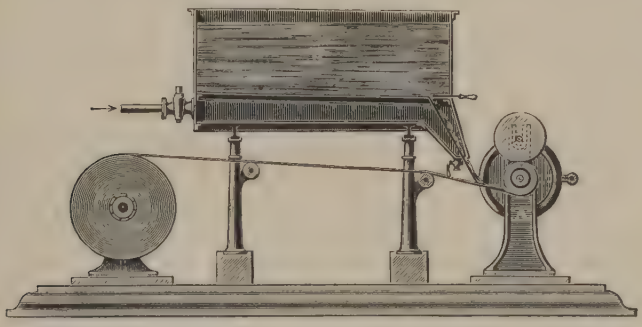


FIG. 128.

cables. These are laid in wooden shoots, afterwards filled with liquid pitch. For this purpose Lessing (Ger. P. No. 98278) prepares the pitch by dissolving it in suitable solvents and separating the solution from the solid portions which are good conductors of electricity; the pitch remaining after distilling off the solvent is a much better insulator than the raw pitch.

A German patent (No. 167166) by Rob. Müller describes the preparation of an insulating mixture from pitch and asbestos.

Mann (Ger. P. 170133) converts asphalt and similar substances into an emulsion by dissolving them in liquid solvents, treating them with soap and an appropriate colloid substance and recovering the solvent.

The Distillation of Pitch for Coke.

Long before the technical importance of anthracene was recognized, attempts were made to obtain further products from the pitch left behind after the distillation of coal-tar. The reason for this was the fact that coal-tar pitch was not consumed in any large quantity, except for patent fuel, and that with only this single opening the article would be very liable to become unsaleable. The idea of carrying on the distillation till all the volatile products were given off and only coke remained (for which there was always a certain sale) was very plausible. The motive for doing so became much stronger as soon as the discovery of artificial alizarin had raised anthracene to the rank of the most valuable component of coal-tar. It was known that the pitch contains some anthracene; and the hope of obtaining it therefrom at a profit seemed justified.

The apparently simplest plan, that of carrying on the process in the tar-still itself to the stage of coke, is not feasible. We have seen, on p. 323, that cast-iron is not well adapted for tar-distilling, and wrought-iron would be burnt away too quickly. Moreover, cutting out the coke would be very costly, and would seriously injure the iron plates. A method proposed by Puls (patented 23rd August 1858, No. 1910), viz., adding earthy substances to the tar, so as to prevent the red-hot residue from adhering to the still, would cause the loss of the coke, and is not worthy of serious consideration.

Hence distilling the tar up to pitch in the ordinary stills, and distilling the pitch in separate vessels, either charging them with it in the solid state, or running it while still liquid into the pitch-oven, cannot be avoided. The oven may be a brickwork muffle, or a fireclay gas-retort, or an iron vessel of some shape or other.

The brick pitch-ovens, which were formerly sometimes employed,[1] will be but briefly mentioned here, as they have not proved practically successful. They were muffle-furnaces, about 15 ft. long, 6 ft. wide, and 6 ft. high to the crown of the arch, fired by zigzag flues running underneath the concave-shaped furnace-bed. At each gable-end there was a working-

[1] Figured and described in Ronald and Richardson's *Chemical Technology*, i., p. 541.

hole, about half-way up, closed during the process. The vapours were carried away by a cast-iron pipe, 90 ft. long, and were condensed by air-cooling. Usually two ovens were built side by side, each was charged with 2 tons of pitch, the doors closed with metal plates fastened like gas-retort covers and screwed down. The fire having previously been lighted, volatile products were soon formed, which were condensed in the cooling-pipe and collected in a tank. The oil first coming over resembled the last distillates from coal-tar; the following portions were more viscid, very dark, and empyreumatic. After about twelve hours, when the distillation was nearly finished, large quantities of heavy yellow vapours appeared, condensing partly to a very thick pasty mass; sometimes they yielded a reddish-yellow pulverulent substance, which on exposure to the air soon turned soft and sticky, and contained much pyrene, chrysene, and other hydrocarbons. When nothing more came over, the two gable-end doors were cautiously opened; the vapours inside the muffle took fire, and the soot adhering to the sides and the arch was burnt. The dense smoke then issuing from the doors was aspirated by a vapour-hood and conveyed to a chimney. The cold current of air caused the layer of coke on the furnace-bed to crack and break up into pieces, the attendant using iron tools to accelerate the process. The coke was drawn out red-hot and quenched with water. It was quite honeycombed, owing to the escape of vapours from the pasty mass. The heat produced by the burning of the soot kept the oven red-hot, so that very little fuel was required to be used for the next operation. One hundred parts of pitch yielded 25 parts of oil, which could be mixed with the creosote oil or sold as a common lubricant, and 50 parts of coke; 25 parts were lost. But these were *maximum* yields; in practice very much pitch was lost by leaking through the brickwork, and hence the yield was smaller than from the iron retorts.

Of later statements upon this subject, dating after the invention of alizarin, we shall first quote a report made by Behrens,[1] upon experiments made by him on a large scale. He employed a cast-iron retort in the shape of a horizontal box 13 ft. long, 3 ft. 8 in. wide, and 3 ft. 8 in. high, constructed

[1] *Dingl. polyt. J.*, ccviii., p. 371.

of 16 flanged plates, bolted together and joined by rust cement. The front and back openings were closed by iron doors and luted with lime-putty. On the top of the retort there was a manhole for charging with solid pitch, and a cock for charging with liquid pitch, and also a safety-valve and a 6-in. pipe for the vapours. The latter was connected with an iron box provided below with a swan-neck pipe to run off any liquid, and on the top with a pipe for carrying away steam and uncondensed vapours into a condensing-worm. The retort was set on a flat arch, which was levelled above and heated from below by a fireplace in front; at the back the flame divided into two parts, returned, through two lower flues on each side of the retort, to the front, and once more, through two upper flues, to the back. At first a little water comes over, especially with damp pitch, and hence cautious firing is necessary to prevent boiling over. But as soon as the pitch is fairly boiling, oily matters condense, and the distillation goes on rapidly even with moderate firing, so that 3 tons of pitch can be distilled in three or four hours and yield 14 or 15 cwts. of oils. The latter are condensed in two fractions — the first as anthracene oil, the second as lubricating-oils. From the beginning, with these arrive water, gases (especially ammonia[1] and hydrogen), benzene, naphthalene, and volatile oils (of sp. gr. 0·97). When two-thirds of the oil have distilled, the formation of coke commences; the mass swells; and if the retort has been fully charged, the fire must now be slackened.

When the production of oil is nearly finished, the more volatile hydrocarbons decrease, but there is even more steam and gases. At last there appears a reddish-yellow resinous sublimate, which gradually ceases, and the evolution of gases ceases also. The retort is now carefully opened, and the gas issuing from it is lighted; otherwise the access of air might cause an explosion. There were obtained :—

Oils containing anthracene	27 to 30 per cent.
„ „ chrysene and pyrene .	
Sublimed reddish-yellow rosin . .	
Coke	48 „ 52 „ „
Gases, steam, and 0·2 per cent. light oils .	25 „ 28 „ „

[1] Watson Smith also has observed the evolution of ammonia in the coking of pitch (*J. Chem. Soc.*, 1884, pp. 144-8).

The crude anthracene oil, on treatment with alkalis, yielded 3 per cent. of an oil soluble in alkalis, and separable again by sulphuric acid, which on distillation gave 8 per cent. of water, then increasingly viscid oils, and, above 360°, a transparent wine-coloured solid mass; a little carbon remained behind.

The following apparatus of Fenner and Versmann for coking pitch has been worked on a large scale. The tar is first distilled in an ordinary wrought-iron still; that shown here (A, Fig. 129) is shaped like a horizontal boiler. B is the condenser for light oils and creosote oil. When the anthracene oil is about to come over, the liquid pitch is run, while still hot, into a series of cast-iron vessels C C C, in which the coking is effected. It passes through the cock *c*, the main pipe D, and the taps *d d d*, into each of the pitch-stills. Figs. 130 and 131 give details of the latter. They are made of cast-iron, and are about 4 ft. in diameter, and 4 ft. 8 in. deep (inside measurement); it is alleged that, when set in the way indicated in the diagram, they will last five or six years, distilling off one charge of 1½ to 2 tons of pitch every three days—one day being occupied in the distillation, and two more in the cooling, emptying, and recharging. A production of 10 tons of pitch per day therefore requires three sets of six cast-iron pots each for the coking-operations. *a* is the cast-iron pitch-still; *b*, furnace; *c c c c*, flues; *d*, pitch-delivery pipe; d^1, stopcock; *e*, condensing-tube for the vapours evolved; e^1 e^1 e^1, branch pipes delivering condensed liquors to the tank; *f*, condensing-chamber; *g*, tank.

The vapours evolved are condensed solely by atmospheric cooling, partly in the tube *e*, partly in the condensing-chamber *f*. The evolution of vapours is greatly facilitated by creating a partial vacuum in the still *a* by means of an exhauster or blower attached to the exit-pipe of the chamber *f*; but no advantage is gained by blowing either hot air or steam through the pitch (*cf.* p. 372). Towards the latter part of the distillation the branch tubes e,^{1} e,^{2} e^3 are successively opened, so as to provide as short and ready a passage as possible for the escape of the condensed substances into the tank *g*. This is essential; otherwise the vapour-delivery pipe *e* is apt to become blocked up by the separation of solid matter.

The distillate of 315° to 370° C. is, according to Fenner and Versmann, very rich in anthracene [this is very doubtful!—G. L.], but little naphthalene or chrysene is present; between

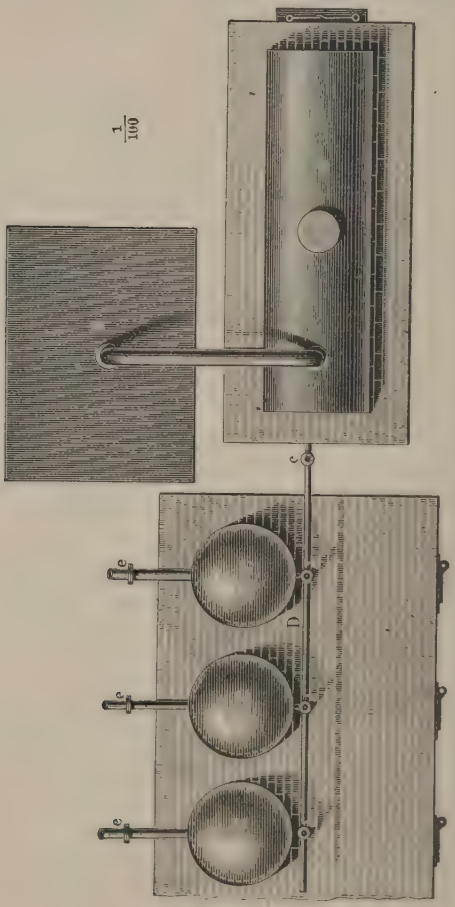


FIG. 129.

260° and 315° the naphthalene is in excess; above 370° anthracene is less abundant, chrysene and other bodies of higher boiling-point than anthracene being the main constituents of

the distillate. On standing, these distillates deposit solid matter, from which rough anthracene is separated by filtration, washing

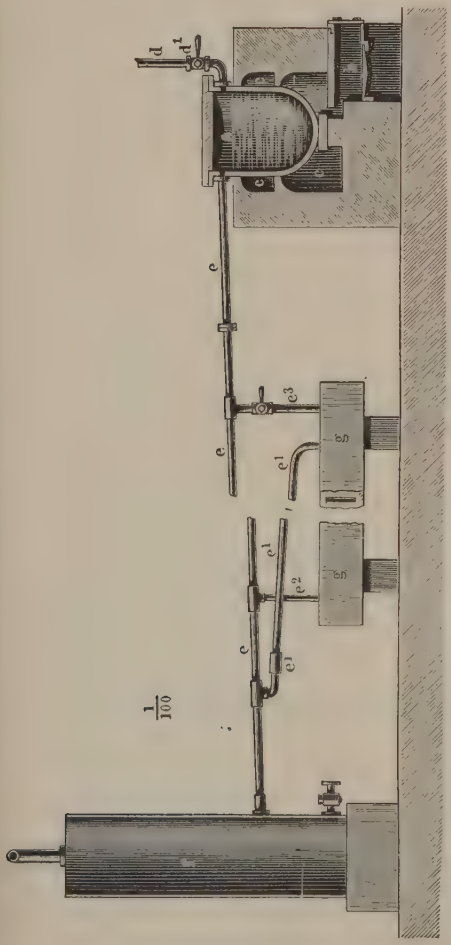


FIG. 130.

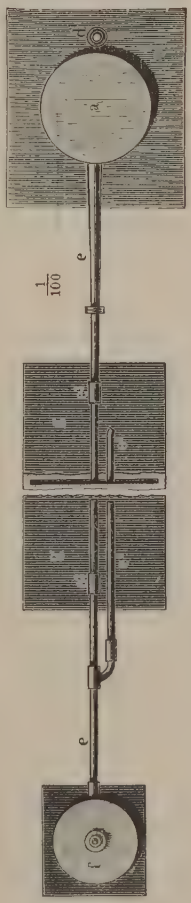


FIG. 131.

with lighter oils, and pressing, as will be described in the next chapter.

This plant may also be used for the distillation of pitch

purchased in that state for the extraction of *anthracene* from it. For this purpose the pitch is broken up into small lumps and, preferably, mixed with oils arising from a previous distillation, or with dry absorbent carbonaceous matter. The object of this is to prevent frothing and the blocking-up of the vapour-delivery tubes on first heating, owing to the presence of moisture in the pitch. The patentees state that, on an average, 2 per cent. of anthracene is thus obtainable from ordinary pitch. As ordinary coal-tar yields about 0·5 per cent. of rough anthracene and 67 per cent. of pitch (this latter corresponding to 1·33 anthracene per 100 of original tar), it follows that the production of anthracene is nearly quadrupled when the tar is coked—*i.e.*, all together, 1·85 per cent. is obtained instead of 0·5 per cent., if the above statement be correct. Unfortunately "pitch-anthracene" has been found to be so much contaminated with chrysene, etc., that the alizarin-manufacturers cannot very well purify it, and will not work with it at any price. Several lawsuits have arisen from this circumstance, and the manufacture of pitch-anthracene seems to have been entirely abandoned. It could hardly be otherwise, as the production of ordinary anthracene in the United Kingdom alone is in excess of the present demand of the whole world (see next chapter). The coke left behind is very good (see below); and the oil from which the anthracene is separated is an efficient lubricator; this is actually the only opening for the pitch-oils in general, until some better method of purifying the pitch-anthracene be discovered.

Watson Smith (priv. comm.) obtained from ordinary hard pitch by distilling, mixing the distillate with mother oils, and redistilling, no more than 0·556 per cent. rough anthracene from the pitch, or 0·33 from the tar.

The proposal of E. Kopp (p. 371) might be referred to this chapter also.

It is asserted that since the introduction of steam in the last stage of tar-distilling all the anthracene is taken out of the pitch, and that it is thus from the outset impossible to work the pitch for anthracene, as there is none in it.

One of the principal difficulties in the distillation of coal-tar pitch, which prevents this operation from being very extensively employed, is that of finding a suitable material for the retorts.

Brick muffle-furnaces leak too much; fireclay retorts require too much fuel in proportion to the quantity of pitch worked up; cast-iron is quickly destroyed by the heat and the pitch, although Fenner and Versmann assert the contrary respecting their construction figured above.

F. von Dahmen and P. Hagyi Ristic & Co. obtained a German patent (No. 166972) for making coke from tar, etc., by running the tar in a boiling-hot state into white-hot retorts, by which process a very dense coke is obtained.

Cyrus M. Warren (Ger. P. 12933, 16th July 1880) proposes distilling tar as usual down to hard pitch, then running into the still whilst hot residues from petroleum-refining, and distilling off once more as much of the oils as corresponds to the weight of the petroleum-residues. From this oil anthracene separates, together with paraffin, which latter is removed by hot-pressing. (It is doubtful whether this plan will furnish easily saleable anthracene; nothing is more dreaded by the manufacturers of alizarin than the presence of paraffin in their anthracene.)

More rational would appear the proposal of Wischin (Eng. P. 1980, 1880), to add gradually, at the last stage of tar-distillation, heavy coal-tar oil, preferably heated beforehand, whose vapours carry away the anthracene without injuring the quality of the pitch.

Watson Smith (*J. Soc. Chem. Ind.*, 1892, p. 119) noticed a distinct smell of *ammonia* when coking tar-pitch, but only on cooling, also in dry air long after the hydrocarbons have passed over. Alder Wright noticed besides this a smell of *cyanogen*.

Kent (Ger. P. 194372) prepares lubricating oil, free from phenols and napthalene, by distilling pitch from water-gas tar and gas oils.

The *coke* obtained by distilling pitch is very good if properly made, but only in that case. This subject has been treated in detail by Behrens (*loc. cit.*). The quality of the coke depends upon the temperature at which it has been made, and upon the length of time during which it has been exposed to that temperature. If both are insufficient, a dull, blackish, compact mass is obtained, with but few cracks. On opening the retort this coke takes fire and burns with a luminous flame issuing

through the cracks of the mass. Even though the coking is somewhat promoted by such burning-out, and the cracks are widened with a crowbar, the quality of the product is very inferior, owing to all pitch-coke, except the very hard-burnt kind, crumbling to dust in the fire. Hence coke that is only burnt out afterwards possesses but very little cohesion; and as it strongly adheres to the sides of the retort, much dust is produced in breaking it up and getting it out. Coke not ignited, having been quenched with water, must from time to time be drenched with water again, as otherwise it easily takes fire. In order to make *hard* coke, the temperature inside the retort, when the red vapours indicating the end of the distillation have disappeared, must be raised to a bright red heat; and this should be kept up for eight hours at least. Thus a complete operation lasts about twenty-four hours. Hard-burnt coke adheres but little to the sides of the retort, possesses great cohesion, and consists of prismatic columnar pieces, which can be got out of the retort almost without using a crowbar. After being once quenched it does not take fire again. It is light grey, very dense, and does not crumble in the fire. Behrens made some experiments with such coke in English iron-works, with the following results. No success was attained in employing it for melting cast-iron in cupolas in lieu of charcoal, or for refining wrought-iron on hearths; in the latter case the slag was not easily separated from the iron. But hard pitch-coke is very good for refining pig-iron in the English way, which is usually done by gas-coke; the refined pig afterwards yielded very good wrought-iron on puddling. This coke is also very well adapted for fusion processes in crucibles.

According to Stavely,[1] pitch-coke contains only 0·11 to 0·12 per cent. sulphur and 2·43 to 2·50 per cent. ashes; it does not crumble even when exposed for months in the open air, as there is no sulphide of iron in it; and it surpasses even the best Durham coke in hardness, density, heating-power, and strength to sustain heavy loads.

[1] *Chem. News*, xliii., 228.

Other uses of Coal-tar Pitch.

Coal-tar pitch is an excellent *reducing-agent* (*e.g.*, for black-ash mixing, for making barium sulphide, etc.), because it is nearly free from ashes and sulphur; but it is mostly too expensive for this purpose, whilst it more frequently pays in the manufacture of ultramarine.

As a factor in the manufacture of *cement-steel* (blister-steel) it has been patented by E. J. Payne and W. Clarke (Oct. 5, 1872).

It is contended that the iron combines more quickly with the carbon from pitch than with that from any other source.

An attempt made by Behrens (*loc. cit.*) to employ the pitch in *gas-making*, by melting it and running it through a bright-red iron tube, yielded, on an average, for 1 kg. pitch, 250 litres of gas, but almost devoid of illuminating-power. It consists mainly of hydrogen, and contains some sulphur, and would therefore be hardly of any value in gas-making.

Balfour and Lane (B. P. 12721, 1886) add from 5 to 10 per cent. of soft pitch to the coal used in the manufacture of illuminating-gas, in order to get more and better gas, richer in benzene, and denser coke, containing little sulphur. The improvement in the quality of gas would seem to be very doubtful.

Kraemer proposed to utilize any excess of pitch by adding it in small portions to coal, coked in ordinary *coke-ovens*. This yields pure coke of excellent quality.

Pitch-coke has recently become a very valuable material for the manufacture of *electric carbons*.

When pitch cannot be utilized in any other way, it can be *burned to lampblack*. The furnaces and condensing-chambers for this purpose are similar to those described on p. 252 *et seq.* for burning tar; only, as the pitch is solid, it must from time to time be thrown upon the red-hot iron plates on which it is to be burnt. No doubt a vessel might be fixed above these, where the pitch would be melted by the combustion going on below, and from which it would be run out continuously by means of a valve in the bottom. According to Thenius 500 kg. of pitch yield 200 kg. of different descriptions of lampblack, and 200 kg.

of coked residue, which is knocked off with hammer and crowbar and used as fuel. Along with pitch any dry alkaline residues from purifying the tar-oils may be burned; but usually none are obtained, as the alkali is employed in aqueous solution.

Testing of Pitch.

Pitch is usually tested for its *softening-* or *melting-point.*

Soft pitch (*brai gras*)	softens at	40°,	melts at	60°.
Moderately hard pitch	„	60°,	„	100°.
Hard pitch (*brai sec*)	„	100°,	„	150° to 200°.

A practical test is kneading a sample between the teeth. If this can be done easily, the pitch is soft; if with more difficulty, it is moderately hard; and if it is crushed to powder, it is hard. Soft pitch is more shining and black than the very hard pitch, which verges upon grey and has less lustre. Sometimes the latter is even a little porous: if it is more so, it is partly coked and cannot be used for patent fuel. The specific gravity of hard pitch is about 1·3.

A test for soft pitch, to see whether it is suitable for patent fuel, is dipping a piece of about 4 in. length and $\frac{3}{4}$ in. diameter for two minutes in water of 60°; when taken out it should bend without breaking. For harder descriptions water of 70° is taken; on the other hand, it is sometimes required that pitch should easily twist at 55°.

I am indebted to Mr F. G. Holmes, of Messrs Burt, Boulton, and Haywood, for the following notes on a method for testing pitch (softening- and fusing-point):—

"Several pieces of pitch are taken from different parts of the sample and cut to the size of a half-inch cube. These cubes are then fixed on metal wires by heating the ends of the wires and pressing them into the pieces of pitch, which are then suspended in a vessel containing about 500 c.c. of water heated by any convenient means, at a uniform rate of 5° C. per minute, as indicated by a thermometer immersed in the water with the bulb about $1\frac{1}{2}$ to 2 in. from the bottom of the vessel.

"The cubes are suspended on a level with the bulb of the thermometer. As the temperature rises the pieces of pitch are taken out from time to time and twisted or squeezed with the

fingers, and the temperature noted at which they assume the following conditions:—

(1) Readily twisting or soft.
(2) Very soft.
(3) Fused.

(1) The twisting-point is when the pitch can be easily twisted round several times.
(2) Very soft, when it yields to a very light pressure of the fingers.
(3) Fusion, when the pitch melts off the wire."

More accurate results are obtained by the following contrivance (originated in France, and also communicated by Mr Holmes). The tin cylinder, Fig. 132, contains a horizontal partition, in which five tubes are inserted, closed at the bottom. The central tube serves for introducing a thermometer, the other four tubes are filled with ground-up and sifted pitch. The sifting must remove both the coarse particles and the dust. The pitch-powder is weighted by an iron disk attached to a pin of definite weight, the perforations in the top cover serving as guides for the pins and the thermometer. The cylinder is now filled with water a little above the tops of the tubes, and is heated over a lamp till the disks sink down into the melted pitch, the temperature being noted at that point.

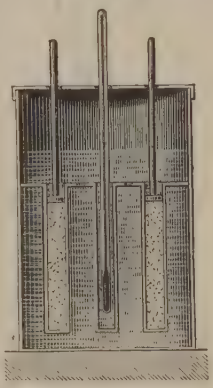


FIG. 132.

Muck[1] moulds the samples into cylindrical sticks, 4 mm. thick and 100 mm. long, which are bent round for a length of 20 mm., so that the shorter limb can be attached by an india-rubber ring to the mercury vessel of a thermometer, whilst the longer limb is parallel with the stem. The whole is immersed in a beaker provided with a mechanical stirrer and filled with water, and this is cautiously heated until the longer limb begins to turn down.

Buchanan[2] sticks a piece of pitch to a thermometer, placed in a dry test-tube and heated in a water-bath. The pitch first

[1] *Zsch. f. Berg-, Hütten- u. Salinenwesen*, 1889.
[2] *J. Soc. Chem. Ind.*, 1894, p. 1098.

softens and then falls off. This happens with hard pitch at 80°, with medium hard at 55°, and with soft pitch at 50° C.

Schenk zu Schweinsberg[1] prepares, from a glass tube 7 mm. wide and 25 cm. long, the apparatus shown in Fig. 133. The lower portion up to *e f* is filled with ground pitch *p*; if too soft for grinding, the pitch is moulded into small pellets. A drop of mercury is poured in, and the narrow part of the tube is drawn out into a capillary (as shown on the right-hand side). A platinum wire *a, b, c, d, q* is attached to it as shown in the figure, the loop at *d* serving for putting in a glass rod, by means of which the whole is suspended in a beaker filled with water, together with a thermometer whose bulb is at the same level as the pitch. The water is very slowly heated, and any gas-bubbles are removed from the glass tube by means of a feather-quill. As the heat increases, the pitch sinters down to about half its original volume. When its fusing-point is reached, this is shown by a swelling up. The commencing fusion is most easily seen in the lower bend and at the point of the tube. The thermometer is now read, to establish the fusing-point, but the heating is continued until the pitch rises in the tube and the drop of mercury sinks down and is enclosed by the liquid pitch, so that the whole of the lower part of the tube is filled with liquid pitch and mercury. This point, at which the temperature is again noticed, is called the "practical" fusing-point; it is below 50° C. for soft pitch, 60° to 99° for medium hard, and above 100° for hard pitch.

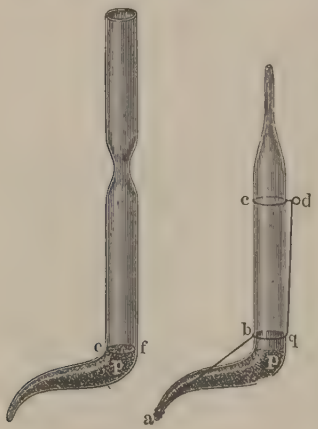


FIG. 133.

Klimont[2] approves of this test, but only when carried out by a person who has much experience with it. He prefers employing an ordinary test-tube, the bottom of which is charged with powdered pitch and which is suspended in a beaker alongside a thermometer. For hard pitch the beaker is filled with

[1] *Z. angew. Chem.*, 1890, p. 704. [2] *Ibid.*, 1900, 761.

glycerine, for soft pitch with water, and it is very gradually heated until the surface is smooth and shining. This is the melting-point. He also describes another method, which must be consulted in the original.

Mabery and Sieplein[1] employ a glycerin bath (Fig. 134), in which is placed a narrow beaker B closed by a cork, through which passes the thermometer C and a metal strip D, $\frac{1}{2}$ in. broad, ending $\frac{1}{2}$ in. above the bottom of B, where it is bent upwards. On this is placed the sample of asphalt or pitch E. This sample must form a slab, 1 in. long, $\frac{1}{2}$ in. wide, $\frac{1}{8}$ in. thick, so that it projects over the strip D. The thermometer should be $\frac{1}{8}$ in. distant from the sample. The heating is continued up to the point where the sample has sufficiently softened to bend down on both sides of the metal support.

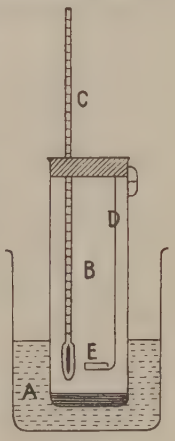


FIG. 134.

Kraemer and Sarnow[2] declare the following method for estimating the softening- or melting-point to be most reliable. Melt about 25 g. pitch in a small tin vessel with level bottom in an oil-bath of similar shape at about 150° C., so that it forms a layer 10 mm. deep. Into this dip one end of a glass tube, open at both ends, 6 or 7 mm. wide and 10 cm. long. Close the upper end of this with the finger, take it out of the glass and allow the pitch contained in the other end to cool in a horizontal position, turning it round all the time. When the pitch is no more liquid, it will occupy a height of about 5 mm. Remove the pitch adhering outside, and pour upon the pitch in the tube exactly 5 grms. mercury, measured off in a small tube provided with a mark. Suspend the tube (or a number of them) in a small beaker, filled with water, place this in a larger beaker filled with water, put a thermometer in the smaller beaker in such manner that its mercury vessel is on the same level as the pitch sample, and heat with a small flame. The temperature at which the mercury breaks through the pitch is noted as the fusing- or softening-point. For samples of a

[1] *J. Amer. Chem. Soc.*, 1901, xx., p. 16; *Chem. Centr.*, 1901, i., 809.
[2] *Chem. Ind.*, 1903, 55.

fusing-point above 90° C., the outer beaker is filled with white paraffin oil, the inner one with saturated solution of common salt or magnesium chloride. The results obtained are rather lower than by the old capillary method, but are quite constant and therefore well adapted for comparison.

H. Bauer[1] describes an apparatus employing the same principle in what he considers a more convenient form.

Wendriner (*Z. angew. Chem.*, 1905, 1946) shows that a very slight percentage of water in pitch causes great irregularities in the fusing-points. Russig (*Chem. Zsch.*, iv., 464, 543; v., 363) considers differences of 2° or 3° in the fusing-points of pitch to be of no moment whatever, since the fusing-point, hardness, and cementing power do not run parallel in pitches of different origin.

Muck (*loc. cit.*) pays much more attention to the outward appearance of the residue. If this is swelled up, the briquettes made from that kind of pitch do not stand the fire, but fall to powder; but if the residue is partially fused, the pitch is good for briquettes. According to his observations, hard pitch nearly always yields a swelled, soft pitch a semi-fused residue, and the latter is therefore preferable.

Köhler cites the following specification for pitch intended for the manufacture of briquettes:—(1) Pieces of $\frac{3}{16}$-inch thickness are placed in water of 60° C.; after this has cooled down to 55° the pitch may be easily twisted without breaking. (2) When carbonized in a crucible before a gas-blast at a bright red heat, it should not leave more than 45 per cent. residue. (3) It should be pure coal-tar pitch, softened with anthracene oil, not with creosote oil or naphthalene (which could be proved by distillation), in which case it fouls the pistons of the presses.

The *viscosity* of pitch-like substances is tested by Tronton and Andrews[2] by means of torsion. A constant torque is applied to a cylindrical bar of the material, and the relative motions of the ends are observed, from which and from the dimensions of the cylinder the viscosity is calculated.

Binder[3] prefers testing the pitch for briquettes by making small briquettes of about an inch diameter with various mixtures, and testing these by means of a specially constructed press,

[1] *Chem. Centr.*, 1905, ii., 1745. [2] *J. Soc. Chem. Ind.*, 1904, 680.
[3] *Chem. Zeit. Rep.*, 1899, 194.

heated by gas. Later on[1] he describes his apparatus more fully. He uses a small cylindrical steel mortar, as employed in the analysis of minerals, heats it to 100° to 150° C., puts the mixture of pitch and sand or coke-powder into it and compresses it by putting on the pistil and giving three or four heavy blows with a hammer.

For more exact tests the real "bitumen," as distinct from "free carbon" (coke) and ashes, is estimated. This can be done in the way usual for testing bituminous coal for the yield of coke, viz., by heating say 1 grm. of finely powdered pitch in a platinum crucible of 1¼ to 1½ in. height, with the lid on, by means of a good Bunsen burner, first gently, till no more smoke and flames issue between the crucible and its lid, then as strongly as the burner will permit. The operation should last about twenty minutes. The crucible is placed in a desiccator and the coke is weighed after cooling; it amounts to from 25 to 50 per cent. of the pitch.

For a direct estimation of the bituminous substances as distinct from "free carbon," in pitch, it is successively treated with hot benzene, carbon disulphide, and alcohol, and this treatment is again repeated. The operation is conveniently carried out by means of a Soxhlet's extracting-apparatus. Since the fine dust easily passes through a filter, it is sometimes preferable to simply boil the pitch in a flask with reflux-cooler and to decant through a filter. The residue left may be considered as "free carbon" (more properly speaking, coke). We refer to the details of this process in Chapter III., p. 426.

Constam and Rougeot[2] estimate in briquette pitch both the coke residue obtained by heating, as above, and by extracting the pitch with bisulphide of carbon. Russig (*Chem. Zeit.*, iv., No. 19) does not approve of this solvent being used by itself, the results being uncertain.

Kraemer and Spilker[3] consider the percentage of bitumen in pitch as the most important test for its briquette-making quality.

Russig (*loc. cit.*) also believes that the estimation of the real bitumen in pitch is the proper test for its suitability for the manufacture of briquettes, but he does not consider the methods

[1] *Z. angew. Chem.*, 1905, 954.
[2] *Ibid.*, 1904, 845; more fully described in Rougeot's thesis, Zürich, 1905.
[3] *Muspratt-Bunte's Techn. Chemie*, 1905, viii., 13.

for this purpose to be sufficiently developed. More particularly he does not think the fusing-point of pitch as a sufficient criterion of its quality (to which opinion Wendriner, in *Chem. Zeit.*, 1905, 543, makes some objections); *cf. supra*, p. 468.

Hodurek (*cf. supra*, p. 426) exhausts the pitch with boiling benzol, thus obtaining a precipitation of "suspended carbon and bitumen." The "suspended carbon" by itself is found by dissolving the pitch in anthracene oil, filtering and only then precipitating with benzol, the "bitumen" being found by difference against the first test.

J. E. Mills (*J. Soc. Chem. Ind.*, 1908, p. 887) quotes the following tests, employed at the U.S. Government fuel-testing works at St Louis, for the testing of briquette pitch. The material is distilled; all coming over below 270° C. is rejected as valueless. The flowing-point should not be below 70°. The smaller the residue remaining on extracting the pitch with carbon disulphide, the more suitable the material is for briquetting. The higher the flowing-point, the better the briquettes stand in the fire; if it is so high that the working of the machines becomes difficult, it is lowered by the addition of heavy tar oils boiling under 270° C.

The distinction between ordinary coal-tar pitch and *blast-furnace pitch*, according to Buchanan (*cf.* p. 465), can be made by determining the amount of ashes. The former never contains above 0·1, the latter 6·8 to 11·1 per cent. ashes. Pitch containing less than 1 per cent. ashes cannot be blast-furnace pitch. No distinction is possible by the crucible test for coke-residues, as they behave similarly in that respect. From hard pitch Buchanan got 38, from medium pitch 30, from soft pitch 26 per cent. coke.

Sometimes coal-tar pitch has to be distinguished from *natural asphalt*. It is generally sufficient to heat the sample in a crucible, when the pungent, acrid vapours from tar-pitch can be easily distinguished from the pleasant, bituminous smell of natural asphalt. The former can also be easily recognised by the green fluorescence exhibited by even dilute solutions in benzol, carbon disulphide, chloroform, petroleum spirit, etc. Malo[1] describes the following process, worked out by Durand-Claye. The sample of asphalt is extracted with carbon

[1] *Ann. des Ponts et Chaussées*, 1879, t. ii.

disulphide, the solution is distilled, and the residue dried at moderate heat until it is hard and brittle on cooling. It is then powdered, and 0·1 grm. is put into a test-tube, into which 5 c.c. of strong sulphuric acid is poured. The sample is thus left standing for twenty-four hours, protected from air, and then 10 c.c. of water is cautiously added from a pipette, avoiding strong heating. The whole is poured on to a filter and is washed with 100 c.c. water. In the case of natural bitumen the filtrate is colourless or faintly coloured, in that of coal-tar pitch it is dark brown. By preparing samples with a varying percentage of pitch, the proportions of a mixture of the latter with natural asphalt can be approximately estimated.

Hauenstein[1] heats 1 grm. of the material to about 200° C.; after cooling, the substance is powdered and mixed with 5 c.c. absolute alcohol. After a short time the presence of coal-tar pitch is shown by a yellow colour of the alcohol, with strong greenish-blue fluorescence, which becomes more pronounced the greater the percentage of pitch.

Donath and Margosches[2] show the presence of any coal-tar pitch in "natural asphalt" by proving the presence of anthracene by Liebermann's reaction, *i.e.*, the red colour (caused by anthraquinone) which is produced by caustic-soda solution and zinc dust. The same authors later on[3] admit that some coal-tar pitches give only traces of this reaction, and Berger[4] asserts that it may take place just in the case of pure Trinidad asphalt and pure petroleum goudron!

Köhler[5] discourses at length on the distinction of natural from artificial asphalt. He controverts also the assertion of Malenkovic,[6] who considers petroleum pitch as being nearer to tar pitch than to natural asphalt.

Toth[7] also speaks on the difficulty of proving artificial beside natural asphalt.

Lignite-tar pitches can be distinguished from others, accord- to Graefe,[8] by the discovery of phenols. Boil 0·2 to 0·5 g.

[1] Dietrich, *Die Asphaltstrassen*, p. 41.
[2] *Chem. Ind.*, 1904, 222; *Chem. Centr.*, 1904, i., 1647.
[3] *Z. angew. Chem.*, 1905, 1106. [4] *Bitumen*, 1905, 5.
[5] *Chem. Zeit.*, 1906, 36. [6] *Chem. Centr.*, 1905, i., 1283.
[7] *Chem. Zeit.*, 1905, 899; *Chem. Centr.*, 1905, ii., 1054.
[8] *Chem. Zeit.*, 1906, 298; *Chem. Centr.*, 1906, i., 1678.

with 5 to 10 c.c. caustic-soda solution, and filter. On the other hand, dissolve a few drops of aniline in 1 c.c. hydrochloric acid and 10 water, add (in the cold) a little solution of sodium nitrite and put a few drops of the mixture to the boiling alkaline solution of the asphalt. If no phenols are present, the liquid takes a yellow colour, but in the presence of phenols, as is always the case with pitches from lignite (or wood), a reddish-brown colour appears, sometimes even a precipitate.

Statistics are only obtainable from Germany. That country formerly produced nothing like the quantity which it consumed for the manufacture of briquettes (*cf.* p. 435), and hence until 1902 had to import a large quantity of pitch, as shown in the following table:—

Year.	Pitch imported.	Pitch exported.	Year.	Pitch imported.	Pitch exported.
	Tons.	Tons.		Tons.	Tons.
1894 . .	29,977	7,712	1900 . .	55,415	4,350
1895 . .	39,916	8,937	1901 . .	59,488	4,613
1896 . .	52,088	9,617	1902 . .	24,266	5,152
1897 . .	48,248	7,099	1903 . .	8,603	4,354
1898 . .	52,700	4,888	1904 . .	8,106	4,074
1899 . .	64,692	4,630			

The strong decline in the importation since 1901 was caused by the development of the recovery of tar in the manufacture of coke (p. 57), and this has led to the consequence that Germany now produces practically all the pitch she requires.

In 1907 Germany imported 20,283 tons and exported 16,892 tons of coal-tar pitch.

CHAPTER VII

ANTHRACENE OIL

ANTHRACENE oil (green oil, green grease, red oil) consists of the highest-boiling portions of coal-tar, starting from the point at which the oils begin to separate solids again (*i.e.*, when the thermometer shows about 270° C. in the vapour) to the end of the distillation. Its boiling-point is between 280° to 400° C. Its specific gravity about 1·1. Its colour is greenish-yellow when fresh, but it turns more brownish by the action of the air. At 60° C. it should be quite liquid, but when cooling down, the crude anthracene separates out in the form of greenish-yellow, sandy crystals. It contains essentially the following bodies—naphthalene, methylnaphthalene, anthracene, phenanthrene, acenaphthene, diphenyl, methylanthracene, pyrene, chrysene, retene, fluorene, fluoranthene, chrysogen, benzerythrene, carbazol, acridine, hydroacridine; but along with these substances, all of which (except methylnaphthalene) are solid and partly only fuse at a high temperature, there is a mixture of liquid, high-boiling oils of which we know as yet next to nothing. Substances containing oxygen (phenols of high boiling-point) are also present; of these α and β naphthol have been distinctly proved to exist in coal-tar. The whole forms a mass rather thinner than butter, with crystalline grains or scales intermixed, of greenish-yellow colour.

The working-up of anthracene oil consists essentially in the separation of the solid from the liquid hydrocarbons by cooling and pressing. The latter go back to the heavy oil, of which the anthracene oil was the last fraction; or they are employed as lubricants, or are redistilled. The solid portion is either sold as crude anthracene or is further purified by "washing."

Simple as the process of making crude anthracene appears,

the different ways in which it is conducted make great differences in the yields of anthracene, which, from the high price of this article, considerably affect the profits of tar-distilling.

The quantity of crystals which make up the crude anthracene is from 6 to 10 per cent. of the anthracene oil. As these crystals contain about 30 per cent. real anthracene, the latter amounts to from $2\frac{1}{2}$ to $3\frac{1}{2}$ per cent. of the anthracene oil.

Currie[1] asserts that a larger yield of anthracene is obtained by adding sulphur to the tar before distilling; a copious evolution of hydrogen takes place. It does not appear that this process is worked anywhere.

The anthracene oils are sometimes divided into two fractions, apparently without much advantage. They are first allowed to rest for some time, so as to cool and deposit the crystallizable substances. Even in summer five to eight days should suffice; but at some works a fortnight is allowed. In any case, much anthracene remains dissolved in the liquid oils, which are therefore often redistilled in order to obtain more. Cooling by means of refrigerating machines hastens and completes the crystallization; but as it also renders the mother oils very viscid, artificial cooling would seem adapted only for the hot season. The cooling is best effected in shallow iron pans, not more than 18 ins. deep; where space is an object, several such may be mounted one above another. It is best not to go below 15° C., as otherwise the rough anthracene comes out too impure.

When the crystallization is complete, the pasty mass, testing about 10 per cent. of pure anthracene, is forced by air-pressure into filters made of strong bagging. Even in this process there are differences; and in 1880 I found at some even very large works long rows of bag-filters of the old shape, in which the oil slowly drains off. A much better plan is the following, often followed by English tar-distillers, the apparatus forming a rough kind of filter-press. A force-pump, or compressed air, forces the paste into a 4-inch main-pipe, *a* (Fig. 135), from which branch off a number of 1-inch T-pieces, *b b*. Over their flanged end sacks, *c c*, made of strong bagging, are tied with string. The sacks are open below, but are at first tied there also. When filled, they

[1] *Chem. News*, xxxi., 175.

are about 1 foot in diameter and 4 or 5 feet long. They hang over a tank for receiving the oil draining off. When the forcing apparatus is set in motion, the sacks are filled with the anthracene-oil paste, of which the liquid portion at once begins to drain off. This goes on slowly, as the oils are viscid; but by increasing the pressure, until the gauge shows at last 1 atmos-

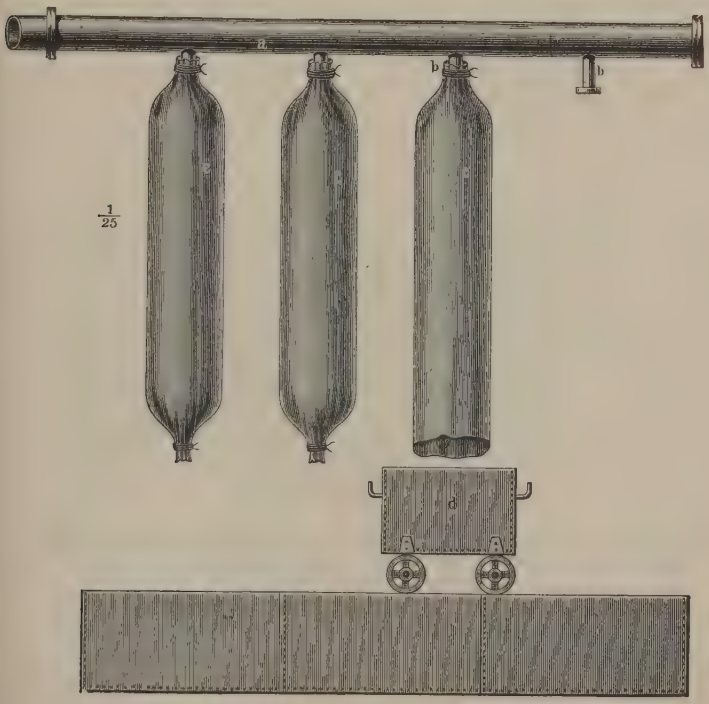


Fig 135.

phere over-pressure, the draining is effected much more speedily and completely, so that the contents of the sacks become nearly dry. Certainly some considerable quantity of the finer crystals is forced through the bagging along with the oils; therefore the latter must be allowed to settle, and the deposit again pressed. When, in spite of pressure, nothing more runs out, the sacks are emptied. For this purpose a small carriage, *d*, is run on a line

of rails underneath each sack in turn; the lower string is untied, and the falling-out of the contents assisted by knocking the sack. The rough anthracene thus obtained usually contains 12, or at most 15 per cent. anthracene by Luck's test.

In Germany filtering-boxes are generally employed, with laths on both the sides and bottom, about an inch apart, covered with rather densely woven jute sacking, where the crude crystals are allowed about a week for draining.

Much more thorough and cleanly is the action of *filter-presses*, of which there is now quite a number of systems. That of Danek (manufactured by Dehne, at Halle) is shown in Figs.

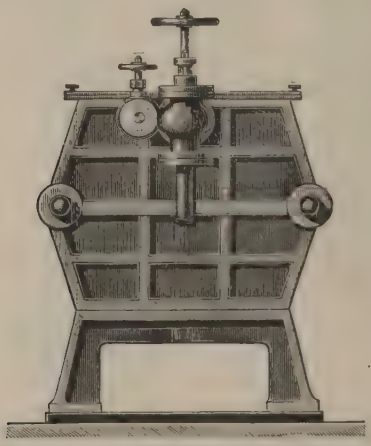


Fig. 136.

136 and 137. It seems unnecessary to give here details concerning the construction and treatment of filter-presses, always obtainable from the makers. The German works visited by me did not get more than 12 per cent. anthracene even with them; at a Dutch works 15 to 18 per cent. was obtained.

Centrifugal machines are also employed, with 1500 or 2000 revolutions per minute, especially for thicker oils. The crude anthracene is either put into sacks made of strong jute, placed close together, or, less preferably, passed directly into the drum of the centrifugal. The work is continued about an hour. When commencing with the crude anthracene from the filters,

the centrifugalled product shows 28 to 33 per cent. real anthracene. It is even possible to obtain 70 or 80 per cent. stuff by washing the product in the centrifugal itself with solvent naphtha or other suitable liquids; but this process causes too much loss, and has been abandoned.

Many factories, in preference to centrifugals, press the preserved product in *hydraulic presses*, either vertical or horizontal. Vertical presses (Fig. 138) are most usual; they are just like those employed at beetroot-sugar works. The rough anthracene is put into cloths and so exposed to a

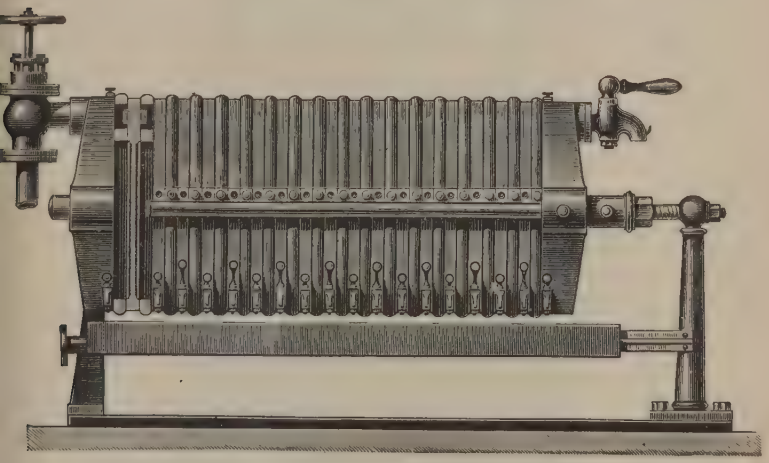


Fig. 137.

gradually rising pressure, at last up to 300 atmospheres, till nothing more runs off. Sometimes, especially if the first draining has been effected in bag-filters only, the first pressing is done cold; and at one of the works visited by me it was asserted that they were getting up to 30 or 32 per cent. anthracene by mere cold-pressing. But mostly that strength is only attained by heating the oils, to make them more liquid and to melt the naphthalene. The application of heat takes place in various ways. Sometimes the oil is warmed before pressing, in a pan with double bottom, by means of steam, and is then pressed in an ordinary hydraulic press. This process will

hardly yield such uniform results as real hot-pressing, especially in winter. In one factory, where I saw this process at work, they came up to 35 per cent. In England the presses are surrounded by a wooden jacket, and steam is passed in during

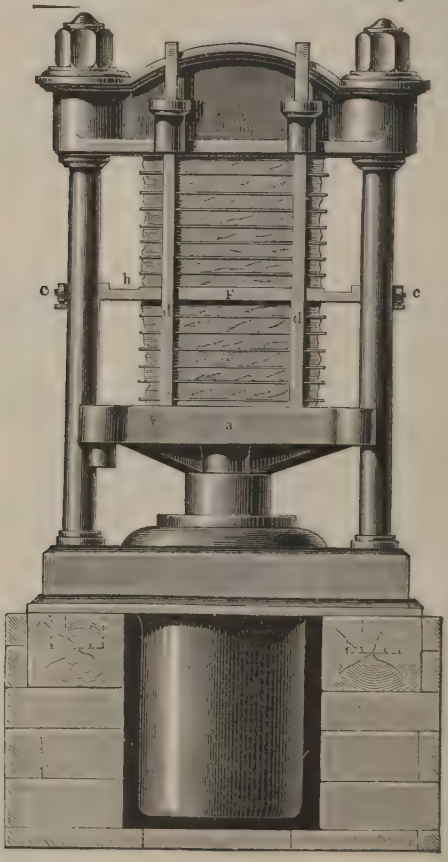


FIG. 138.

this operation. This process is not very cleanly; and the redistillation of the pressed oils is made more troublesome by the admixture of liquefied steam. Far the best, although more costly to erect, are presses similar to those used in the stearine-

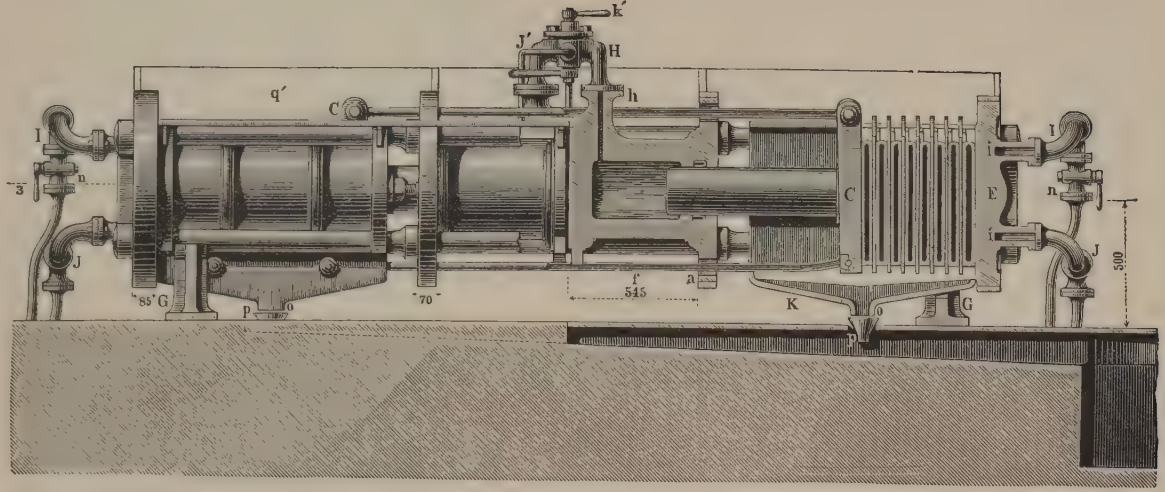


FIG. 139.

manufacture, whose hollow plates are *heated by steam* to about 80° C. The form here shown (Fig. 139), of the horizontal shape generally used at stearine-works, is that employed at most German and Dutch tar-works. This kind of press is very efficient indeed, but it is rather troublesome to charge and discharge. Much more convenient is a press which I saw at a large English tar-works. It is a vertical press, each plate being hollow and heated by a steam-pipe joined to it by a steam-tight socket, just like the plates in the horizontal presses. Each plate is at either side provided with a pin, sliding in slanting grooves worked in the sides of the perpendicular framework. When the ram rises the plates are all raised, and are eventually subjected to as much pressure as is desired; but when the ram descends, each plate is arrested at a short distance from the next by the pins being caught and stopped, so that finally the plates appear fixed at equal intervals, leaving spaces between for introducing the cloths filled with crude anthracene.

According to Kraemer and Spilker (*Muspratt-Bunte*, viii., 67), centrifugals work best, both with respect of cheapness and of removing the oil from the crystals. A filter-press of 24 chambers and 1 square metre section, in twelve hours yields about 2 tons pressed stuff; a vacuum filter with 3 square metres filtering surface, from 2 to 3 tons; a centrifugal with a drum of 3 ft. diameter, 1½ to 2 tons. Preferably the main quantity of oil is removed by a filter-press or vacuum filter, and the remainder by a centrifugal. The quality of stuff obtained by this process is about the same as that of cold-pressed stuff, but of course inferior to the hot-pressed crude anthracene.

Scholvien (Fr. P. 335013) fuses the crude anthracene completely (at 100° C.), and cools down to 50°, whereupon the crystalline mass is drained and centrifugalled, thus obtaining directly anthracene of 45 to 50 per cent. The German patent granted for this process (Ger. P. 111359) was abandoned in 1902.

Catchpole & Catchpole (B. P. 17641, 1903) purify naphthalene and anthracene by a "sweating process," *i.e.*, by heating on a porous surface nearly to the fusing-point, viz., 70° C. for naphthalene, 200 for anthracene, in which process the less fusible impurities are removed.

The *oils draining from rough anthracene* in the presses, etc.,

are sometimes added to the creosote oil sent out for pickling wood; or else they are melted up with hard pitch in the stills in order to make soft pitch, refined tar, etc. (p. 441); sometimes they are sold at a higher price as lubricants. It is most rational to distil them once more in ordinary tar-stills, in order to recover more anthracene, which no doubt previously existed in the oils, but has been kept dissolved by the liquid components, and hence can be obtained (although but partially) only by a new fractionation. In other places the oils are only kept for several months, and the newly formed deposit is collected. E. F. R. Lucas[1] runs the tar-oil that distils between 260° and 360° (undoubtedly after separating the anthracene) through red-hot tubes filled with bricks, and distils the dark oil formed thereby; the oil distilling at 360° is rough anthracene. Almost the same proposal has been again patented by Hardman and Wischin (No. 4517, 7th November 1878), who substitute coke for bricks. At the present time processes of this kind have very little chance of financial success (*cf.* pp. 141 *et seq.*).

A. M. Graham[2] describes the following process as the most suitable from practical experience on the large scale for extracting the anthracene from the filtered oils, which are frequently allowed to accumulate to an inconvenient extent, because the anthracene obtained from them is generally so impure as to be unsaleable. Fractional distillation, retaining only that portion of the distillate which comes over between 300° and 360°, is difficult and expensive. He prefers distilling, say, 1500 galls. of the filtered oils in a perfectly clean tar-still, free from tar and pitch, until crystals of anthracene begin to appear in the distillate on cooling. The distillation is then stopped; and after the temperature of the remainder has been sufficiently reduced, it is run out into a tank and allowed to cool, when the anthracene crystallizes out in large quantity. A second and a third operation can be performed in this way; but usually it is found that the oil is sufficiently exhausted in one operation. The solid portion deposited in the tank will be found, after filtering and pressing, to contain at least 17 per cent. of real anthracene; and this can be easily raised to 36 per cent. by fractional distillation or by washing.

[1] English patent, 24th January 1874.

[2] *Chem. News*, xxxiii., pp. 99, 168.

Watson Smith (priv. comm.) was able to recover from the pressed oils, after treating them, hot, with a little concentrated sulphuric acid and caustic alkali, a large quantity of anthracene by repeated distillations. The last oil boiled at 260° to 290°; the fraction distilling between 260° and 280° remained quite colourless after long standing; it had a pleasant hay-like smell, and the sp. gr. 1·04. It is miscible with paraffin oil and animal oils, and dissolves a considerable amount of tallow. It is also by itself a good lubricant. He could also isolate 0·28 to 0·45 per cent. crude anthracene cake from ordinary creosote oil, sold for pickling; even in the light oil, traces of anthracene were found.

Boleg[1] distils anthracene oil under a pressure of 4 or 5 atmospheres, which yields a bright yellow and mild-smelling oil, much preferable to ordinary anthracene oil. This process also admits of obtaining more anthracene, as well as chrysene and pyrene. When working at 10 or 12 atmospheres, benzol can also be obtained, but this would not pay at the present prices. The pitch remaining behind can be used in the ordinary way. The apparatus (Fig. 140) shows a retort, A, of various shape and size, heated by a steam-jacket or an open fire, or, preferably, as shown here, by Th. & A. Frederking's system of superheated steam (Ger. P. 63315). B is an automatic valve, regulated so as to allow the vapours to pass over to the condensers at a certain pressure. C is a preliminary cooler with a water-jet, by which the danger of explosion or fire is minimized. D condenser, E a Florentine flask for separating the water and oil. The retort A contains a feed-pipe *a*, running-off pipe *b*, steam-coil *c d* (cast into the sides of the vessel), perforated steam-coil *e* for open steam, inside coil *g i* for indirect steam, *f* thermometer or pyrometer, *h* and *l* pipes for cooling water, *m* ditto for the preliminary cooler, *n* waste-pipe for cooling water, *o p* waste-pipe for gases, *q* tap for the lighter oils continually fractionated in the condenser, *s* pipe for the heavy oils, *r* waste-pipe for condensed water.

The retort is two-thirds filled, the valve B is regulated for the desired pressure, and the heating is commenced by means of the steam-coils *c d* and *g i* or one of these. At first ordinary steam of 6 or 7 atmospheres is used, afterwards superheated steam. If open steam from *e* is to be used, it should be super-

[1] *Chem. Rev. Fett- u. Harzindustrie*, 1898, pp. 94 and 97.

heated to the temperature of the retort; but this should not be done before the contents of the retort are quietly boiling.

H. Günther (Ger. Ps. 9566 and 11930) employs the filtered oil for manufacturing *black printer's ink*. It is to be boiled with 10 per cent. of cupric chloride, which imparts a blackish-brown colour to it. The varnish is composed of 40 parts pitch or asphalt, 28 rectified oil of turpentine, 2 aniline violet, and 24 coal-tar oil.

The Rütgerswerke (according to *Chem. Zeit. Rep.*, 1907,

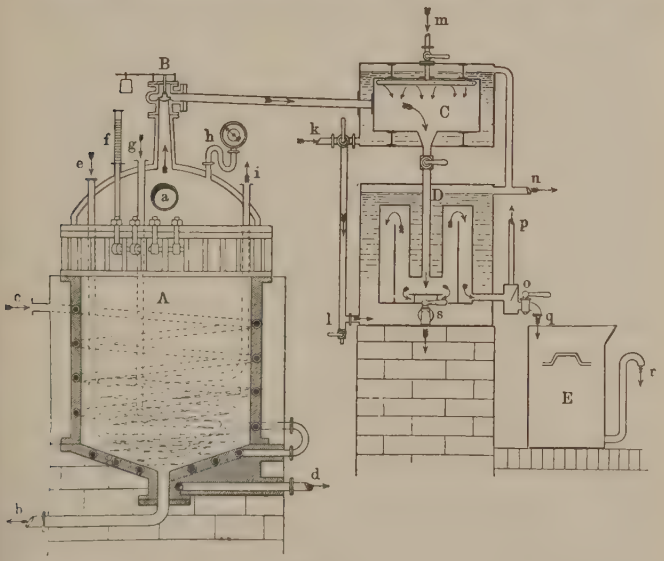


FIG. 140.

p. 129) make anthracene oil *inodorous* by two methods: first, mixing with oxides or hydroxides, or salts of heavy metals, adding an alkali, heating up, passing steam through the mixture for a certain time; second, mixing the oil with formaldehyde or acetone, or preferably a mixture of both, heating, and passing steam through for some time.

Carbolineum.

This name was given to heavy coal-tar oils, used for the preserving of timber, by Avenarius, who for this purpose treated

anthracene oils by gently heating, agitating, and passing in chlorine gas, which is to deprive it also of its unpleasant smells (Ger. P. 46021). This special product is known as "Carbolineum Avenarius" or "Avenarine," but the name of "carbolineum" in Germany is given to many other coal-tar oils or preparations serving for the same purpose, since the original article has been found to be very useful indeed for this purpose.

Some of these oils are of much lower specific gravity, and really belong to the "creosote oil," to be treated in Chapter VIII. Filsinger (*Chem. Zeit.*, 1891, 544) reports upon some of the "carbolineums" of trade, whose specific gravity, with one exception, was between 1·046 and 1·108, and which ought not to have gone under that name. According to Hodurek (*Oest. Chem. Zeit.*, 1904, No. 16) good carbolineum should have a specific gravity not below 1·120; it should not begin to distil below 230° C.; its inflaming-point should be above 120° C.; its viscosity should be as great as possible, the colour red-brown, and no solid matter crystallizing out. Sometimes ordinary green anthracene oil is purposely coloured red-brown, to resemble real carbolineum, by adding colouring matters, or filtered tar or pitch. Timber soaked with real carbolineum retains its nut-brown colour for a long time, but timber treated with oils containing tar or pitch soon get darker and less pleasant looking.

Hodurek believes that the treatment with chlorine, prescribed by the Avenarius patent, is both useless and inefficient. He found as much chlorine in the original oil (0·18 per cent.) as in Carbolineum Avenarius (0·16 per cent.), and in both oils the aqueous extract showed just the quantity of NH_3 corresponding to the Cl present. The proportion of acids (phenols) in good carbolineum amounts to 10 per cent. against 5 to 7 per cent. in ordinary anthracene oil. According to him, all the above-mentioned good qualities can be imparted to coal-tar oils without the application of any patented process, by simply applying a suitable fractionation during the distillation of the tar.

Recently there is found in the German trade an article, sold as "Inodorous antinonnin-carbolineum," which consists of potassium dinitro-cresylate.

Graf & Co. (Ger. P. 63318) make similar oils by treating wood-tar or coal-tar oils with ozonized oxygen or air.

Herborn (B. P. 3922, 1901) obtains a product equal to the "Carbolineum Avenarius" by shaking up anthracene oil with 3 per cent. hydrochloric acid and 2 per cent. of a saturated aqueous solution of zinc chloride. The product is reddish-brown, without smell, and contains 2 per cent. chlorine.

The article sold as "argon" seems to be identical with carbolineum. "Barol" is carbolineum containing some copper compound. "Phenola" is another name for it.

Emma Homann (Ger. P. 154034) employs Carbolineum Avenarius + 2 per cent. soft soap + 1 per cent. cupric sulphate as a protection for trees against "tree-cancer" and the ravages caused by animals.

Knoll & Co. (Ger. P. 175384) obtain permanently liquid high-boiling coal-tar oils by the addition of high-boiling distillates from juniper tar or other wood-tar, or distillations of bituminous masses, like ichthyol oils.

Hübsch reports in a Silesian paper that a human body which had been buried in a coffin impregnated with carbolineum, on being exhumed after two years, was found to be altogether mummified.

Nördlinger (*Pharm. Zeit.*, 1907, p. 1097) tests carbolineum and similar oils by absorbing it in scraps of porous paper, estimating the loss of weight by volatilisation of the lighter oils and extracting the residue with ether.

G. Blass & Sohn (Ger. P. 177249) employ anthracene residues for converting liquid tar into a solid mass.

An important use of anthracene oil is that for *removing the naphthalene from illuminating gas* (Bueb's process), and thus preventing the stopping up of gas-pipes by naphthalene crystallizing in them (*J. Gasbeleucht.*, 1902, 516, 872; 1903, 45). The oils are most suitable for this purpose when cooled down, and the less distillates up to 270° C. they contain. Thus anthracene oil of sp. gr. 1·11, according to Hodurek (*Oest. Chem. Zeit.*, 1904, No. 16), at 28° C. dissolved 22½ per cent. of naphthalene, but when from the same oil the oils distilling up to 270° were removed, this distillate dissolved only 3 per cent. naphthalene (oils from lignite tar dissolve up to 33 per cent. naphthalene).

Since the anthracene oil used in Bueb's process would take out of the gas some of the benzol vapour, so important for its illuminating power, it is now usual to add to the anthracene oil

used for washing the gas, 4 per cent. benzol. In this case the gas passing through the washer neither gives up nor takes up benzol from the washing oil at the proper temperature.

Purification of the Pressed Anthracene by Washing.

Formerly at most works the anthracene turned out by hot-pressing only came up to about 30 to 33 per cent. in winter, and 33 to 36 per cent. in summer. In 1908, the rough anthracene was sold in Germany at 40 per cent., to which point it would appear it can now be brought without any difficulty. At one German works I was credibly informed that they got up to 50 or even 52 per cent., without any washing with naphtha, by three successive pressings, namely, 12 per cent. by the filter-press, 32 per cent. by the cold hydraulic press, and 50 to 52 per cent. by the horizontal steam-heated press.

Such work, however, is decidedly exceptional, and can be explained only by differences in the fractionation during the distillation of the tar. The great majority of tar-works obtain such rich anthracene only by *washing, i.e.*, treating with solvents, of the impurities. As such, carbon bisulphide and alcohol have been thought of, but have hardly ever been used, on account of their cost, their volatility, and the danger of fire. The *solvent naphtha* which is obtained on rectifying the light tar-oils, and essentially consists of xylenes, pseudocumene, and mesitylene, is very extensively employed. It distils between 120° and 190°, as we shall see in detail in Chapter XI. In this naphtha, especially phenanthrene, is much more soluble than anthracene, but the carbazol (of which there is about half as much present as of real anthracene) is not removed, but remains behind with the anthracene. In England, petroleum spirit of not more than 90° boiling-point is frequently used; that boiling at 100° dissolves too much anthracene. Creosote oil is also sometimes employed, as we shall see.

Before washing, the rough anthracene cake should be ground up into fine powder, which must also be done for sale. The grinding is effected by any sort of machine, such as horizontal mills, edge-runners, studded rollers, Carr's disintegrators, etc. The powder is usually stirred up with the naphtha in tight iron boilers, vertical or horizontal, fitted with a mechanical agitator and with a steam-jacket or an interior steam-coil. This is done

for several hours, gentle heat being applied; and the whole is then forced by compressed air into a filter, consisting of an iron box with an inner perforated false bottom, covered with canvas, where the solution is separated from the solid parts, the separation being greatly facilitated by the air-pressure. To avoid danger of fire, the filters, the tanks for receiving the oils, etc., must not communicate with the outer air. It would seem advisable to employ an arrangement sketched in Fig. 141: *a* is the dissolving-boiler with its agitator; *b*, the filter, with the manhole *c* for removing the anthracene; *d*, the vessel for receiving the solution of the impurities in naphtha; *e*, an air-pump, aspirating the air from *d* and forcing it into *a*. Thus the whole of the paste is forced through the pipe *f* into the filter *b*, and the solution through it into *d*. In this way the same

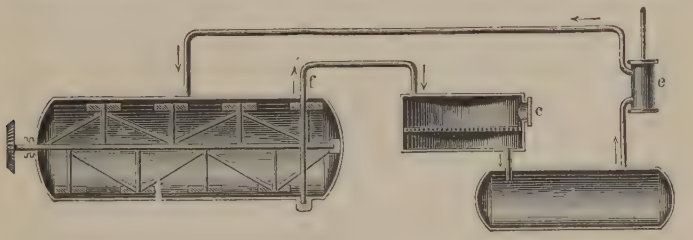


FIG. 141.

quantity of air is always circulating, and a loss of naphtha is avoided as much as possible. Or else the mass may be treated in a centrifugal machine.

The *once-used naphtha* is always recovered, except the inevitable loss, by distilling the solution. The *residue* remaining in the still—consisting mainly of phenanthrene, along with some anthracene, methylanthracene, naphthalene, phenol, and unknown liquid lubricating-oils—is mostly not used for anything except burning to make lampblack (p. 295), for which it is very suitable; but care should be taken that no water remains mixed with it. From this residue, as well as from other products of coal-tar distilling, *pure phenanthrene* might be produced in large quantities, if this substance should ever become the starting-point for other useful products; at the present time it has practically no commercial value. We come back to this point at the end of this chapter.

Some anthracene-refiners recover, by fractional crystallization, the anthracene, of which there is sometimes as much as 8 per cent. in these residues; but the majority seem to think this process too expensive, especially as this anthracene is always contaminated with methylanthracene.

The process employed at one of the largest English tar-works is as follows:—The hot-pressed anthracene is ground up, and is well-mixed in a closed machine with hot solvent naphtha, at a temperature of 77° C. The mixture is allowed to cool down to 21° C., and is now submitted to strong hydraulic pressing. In order to avoid escapes and danger of fire, the press is enclosed in a casing. The press-cakes are heated in a 3-ton still up to the melting-point of anthracene, the vapours being condensed in a small worm; and the melted anthracene is run out and solidified in iron boxes. The solution running out of the hydraulic presses is distilled in ordinary light-oil stills, and the distilled naphtha is used over again for washing anthracene. The residue remaining in the still is first treated for the extraction of some anthracene, by a process said to be very simple, and is then either burned or worked into the creosote oil.

The washing with naphtha yields a product of at least 45 or 50 per cent. real anthracene, and with proper care upwards of 50 per cent.; the highest amount formerly obtained was 70 per cent., and refers to the above-mentioned article that had been previously brought to 50 per cent. by three pressings. Some manufacturers, during recent years, have got up to 80 or even 85 per cent., but mostly without commercial success Quite recently methods have been worked out for attaining that strength in a better way (see below). On the other hand, some makers only get at most 30 or 40 per cent., by treating the rough anthracene, merely purified in the centrifugal machine or filter-press, with naphtha and then submitting it to hydraulic pressure. Hence the former process seems more rational than the latter.

At one of the largest English works they wash first with *crude solvent naphtha* (*i.e.*, the second distillate of the light-oil still). As much as 56 or 60 per cent. anthracene is said to be obtained in this way.

Perkin[1] prefers washing with *petroleum-spirit*, boiling between

[1] *Wagner's Jahresber.*, 1879, p. 1068.

70° and 100° C., which dissolves less anthracene than coal-tar oils, and yet removes the impurities sufficiently. Coal-naphtha sometimes dissolves 7 or 8 per cent. by weight of anthracene, which is difficult to recover. The following table shows the solubilities of anthracene and some other bodies in petroleum spirit and benzol:—

	Petroleum spirit. B.p. 70° to 100°.	Benzol. B.p. 80° to 100°.
Anthracene	0·115	0·967 per cent.
Phenanthrene	3·206	21·94 „ „
Carbazol	0·016	0·51 „ „
Dichloranthracene	0·137	0·62 „ „
Anthraquinone	0·013	0·166 „ „

Creosote oil is also employed for washing anthracene. Some believe that it is not a proper reagent for this purpose, as it dissolves more anthracene than phenanthrene, etc.; but this must be erroneous, at all events with proper manipulation, since several tar-distillers employ creosote oil with great advantage, and some even believe this to be a valuable secret. In this way 40 per cent. anthracene can be obtained by the following process, which I have seen used with great success:—The first crude crystals, testing, say, 10 per cent. pure anthracene, after draining, are mixed with an excess of creosote oil at a temperature of 80°. The mixing being quite complete, the mass is allowed to cool down to 40°, and the crystals then obtained are subjected to hot pressure, when they will yield 40 per cent. anthracene, the creosote oil having dissolved far more of the impurities than of real anthracene. The tepid mother liquor is allowed to cool down to 25°, and thus a second crop of poorer anthracene crystals is obtained; and a third quality is got by allowing the second mother liquor to cool down to the ordinary temperature. The second product is put into the still, where the press-oil is distilled once more; the third product is treated along with fresh crude 10-per-cent. anthracene.

At a large tar-works this process is managed as follows:—1200 kg. of tar-anthracene (got direct from the anthracene oil), and 600 kg. of "oil-anthracene" (obtained by redistilling anthracene oil), both of them cold-pressed, are mixed in a mechanical mixer, provided with a steam-coil, with 1000 kg. of creosote oil, free from naphthalene (the first eighth in the distillation of the tar). The mixture is first heated to 80° C.,

and is then allowed to cool down to 40° or 35°, according to the season. From the mixer the paste runs on to open vacuum-filters, placed on a wrought-iron boiler, evacuated by means of a Körting's injector. The contents of the filter are put into sacks and pressed cold at 80 atmospheres' pressure; the residue is immersed with the sacks into water of 50° C. slowly heated to 75°, then at once brought back into the press and pressed at 200 atmospheres, renewing this pressure twice or three times. Thus the oil-anthracene, which contains much methylanthracene, yields the latter almost completely to the solvent, and the result is very pure anthracene of 40 or 45 per cent.

At another tar-works the process is as follows:—The rough anthracene is first passed through a filter-press, and then through a hydraulic press enclosed in a steam-casing. It is now washed with creosote oil in a steam-jacketed pan, with very well-designed horizontal agitating-gear, which thoroughly mixes up the warm liquid with the crystals. The mass is now filtered by means of a vacuum, the same air continuously circulating, as I had already proposed in 1880 (*cf.* p. 487, Fig. 141). The anthracene thus gets up to 45 per cent.

It is especially contended that the washing with creosote oil removes that most disagreeable impurity in anthracene, viz. *paraffin*, which differs from ordinary paraffin by fusing at a much higher temperature, and is little soluble in either petroleum spirit or naphtha. Even a little of it suffices for disturbing the filtrations necessary in the subsequent operations; it resists pretty completely all the chemical processes to which anthracene and anthraquinone are subjected, and as it melts during the process of oxidizing the anthracene to anthraquinone, it is very troublesome. It has been stated[1] that the paraffins can be removed by dissolving the crude anthracene in a steam-jacketed vessel in 1·2 parts by weight of creosote oil distilling between 220° and 330°, and previously freed from phenols by washing with caustic soda. The solution is stirred till cold, the cooling being promoted by a stream of water, and the magma is pressed in a filter-press. The anthracene thus gets up from 28 to 36 or 40 per cent. by Luck's test; but it is often *not* quite free from paraffin.

Owing to the great danger of fire, the washing of anthracene

[1] *Fischer's (Wagner's) Jahresber.*, 1876, p. 466.

and the recovery of the naphtha ought to be performed at some distance from the other buildings, and not in very large apparatus.

The purification of anthracene by washing is frequently carried out, not at the tar-works, but by special anthracene-refiners or at the alizarin-works. The latter does not seem very rational—first, because this operation is much more in the style of tar-distilling than in that of colour-making, involving as it does the danger of contamination and of fire for those expensive products ; secondly, because the tar-distiller can manufacture and recover the naphtha more cheaply than the colour-manufacturer.

A peculiar anthracene-purifying process was employed for some time at Perkin's alizarin-works, and communicated, under the obligation of secrecy, to one of the largest German works. The secret was even kept for years after the process had been proved to be unsuitable and had been discontinued. It is now known of what it consisted.[1] Anthracene is mixed with *caustic potash* and a little lime, and is distilled out of cast-iron gas-retorts, or wrought-iron retorts, 4 feet wide by 7 feet long, heated by flues below the bottom and along the side, and protected at the bottom against the direct action of the fire by fireclay slabs. These are connected by iron elbow-tubes with shallow iron boxes, in which the distilling anthracene condenses without further cooling. The covers of these boxes are put on loosely, so that the gases evolved at the same time can escape and may even take fire without doing any harm. Caustic soda cannot be employed, because its fusing-point is too high ; and as that of caustic potash is too low, quicklime is added. Two hundred kg. of anthracene are ground up with 60 kg. Montreal potash and 12 kg. quicklime, during which operation the smell of ammonia is often perceived. The mixture is distilled at a low red heat. When this mass is diluted with water, a green solution is obtained which deposits greenish-blue flocks of extremely disagreeable odour. After the distillation the retort contains a porous, wax-like substance which takes fire on contact with air and deposits a sublimate of carbazol in the cooler parts. In fact this body was discovered by Graebe and Glaser in this manner, and does not seem to be easily obtainable in

[1] Auerbach, *Das Anthracen*, 2nd ed., p. 11 ; Perkin, *loc. cit.* ; *Fischer's Jahresber.*, 1885, p. 467.

any other way. The distillate from the retorts forms solid yellow pieces, containing about 40 per cent. real anthracene. From the residue in the retorts the caustic potash can be recovered by dilution with water and boiling with lime, or the residue is carbonized, and used over again as crude potash; but unless a flue-dust chamber is interposed between the grate and the chimney, a great deal of potash is carried away by the draught as fine dust. The distillation with caustic potash is said to destroy the chrysene; but the destruction seems to extend to the anthracene, as shown by the following figures:—600 kg. of 31-per-cent. anthracene cake were distilled with 180 kg. caustic potash and 36 kg. lime; the result was 380 kg. 44-per-cent. anthracene, equal to a loss of 17½ kg., or 10 per cent. When the enormous quantity of fuel for heating and the serious wear and tear of the retorts are considered, it becomes apparent that this process is much too costly. But the anthracene purified in this manner is the best material for preparing chemically pure anthracene; *cf.* p. 197 (Auerbach, *loc. cit.*).

It is sometimes asserted that pitch-anthracene suffers a considerable loss in this operation, but tar-anthracene none at all (?).

Perkin (*loc. cit.*) states that in this process no more anthracene is lost than in distilling without potash, but 40 or 50 per cent. of the impurities are removed. The phenols, he states, are retained in the residue, also a non-volatile compound of carbazol, of which sometimes as much as 10 or 12 per cent. occurs in crude anthracene; so that the distillate consists essentially of anthracene and phenanthrene. The alkaline process is indispensable for the manufacture of alizarin by means of dichloranthracene; and all crude anthracenes, even the worst, yield the same good quality. Anthracene, washed before distillation with naphtha and petroleum-spirit, yields again after distillation a considerable amount of impurities to those solvents (probably phenanthrene). If the process possessed all these advantages not counterbalanced by any drawbacks, it is difficult to understand why it has been abandoned.

In 1884, at a large alizarin-works, I saw a process somewhat resembling that just described, viz., *fusing* (but not *distilling*) the anthracene, previously brought up to 50 per cent. by wash-

ing, with caustic potash (not to be replaced by caustic soda); the carbazol is thus removed as a potassium salt, and the anthracene comes up to 60 per cent.

By washing the anthracene distilled or fused with caustic potash, solvent naphtha, etc., in the manner described, pp. 486 *et seq.*, the percentage of pure anthracene can be brought up to 70 per cent., or, as has been asserted, 80 or 90 per cent.; but the alizarin-makers do not seem to be inclined to pay the extra cost of such purification.

C. Caspers (B. P., May 9, 1873) proposes the following purifying process:—Well-pressed anthracene cake is mixed at from 12° to 15° C. with its own weight of *paraffin oil*, which dissolves napththalene, phenol, cresol, etc. The residue is washed several times with paraffin oil (always at or below 15°), and last of all with methylated spirit, pressed, and dried at 100°. The product is said to contain 85 or 90 per cent. of anthracene fusing at 190°. This can be further purified by fusing and heating to 205°, when a dark green crystalline mass is formed, containing 95 to 97 per cent. anthracene, and yielding perfectly pure anthracene by sublimation (?). If the crude anthracene contains higher fusing bodies, as pyrene, chrysene, etc., the washing with paraffin oil is conducted at such a temperature that the anthracene is dissolved, whilst chrysene, etc., remain behind; on cooling the clear solution down to 15°, the anthracene separates and is purified as above. (I am not certain that this process has been adopted anywhere.)

Remy and Erhart (Ger. P. No. 38417) stir 100 parts crude anthracene with 150 *oleic acid*, heated to 100° or 200°, until almost entirely dissolved. On cooling the anthracene crystallizes almost pure, and is separated from the adhering fatty oil, first by filtering, etc., afterwards by saponifying with alkali or washing with petroleum.

The Chemische Fabriks Aktien-Gesellschaft at Hamburg (Ger. P. No. 42053) obtains almost pure anthracene, especially free from carbazol (which resists the other solvents), by washing the crude anthracene with the mixture of *pyridine bases* obtained in purifying light coal-tar oil, in which a certain proportion of benzol will do no harm. One part crude stuff is treated on a steam-jacketed mixer with 1½ or 2 parts of the basic mixture and allowed to cool and crystallize. In lieu of

pyridine bases, the higher-boiling aniline and quinoline bases may be employed, diluted with the same volume of solvent naphtha. Crude anthracene of 33 per cent. yields with pyridine bases an article of 80 per cent., or with aniline and solvent naphtha 75 per cent. The advantage of the pyridine as solvent is principally this: that it removes the carbazol, whereas benzol and naphtha leave this with the anthracene and remove mainly but phenanthrene. At ordinary temperatures 100 parts of benzol and its congeners dissolve 1 to 1·5 anthracene, 1 to 2 carbazol, and 30 to 35 phenanthrene. By means of these solvents no higher strength than 50 to 60 per cent. real anthracene can be obtained, and the carbazol must, if necessary, be removed by subliming or distilling over caustic potash, which is a very troublesome operation and carried out only at some colour-works (*cf.* p. 491). But the pyridine bases at ordinary temperatures dissolve 2·3 per cent. anthracene, and 22·0 per cent. carbazol, and 35 per cent. phenanthrene. Thanks to this behaviour, by recrystalling normal, well-pressed anthracene with one and a half times its weight of pyridine bases, we obtain anthracene testing upwards of 80 per cent. The apparatus for this object consists of iron cylinders, horizontal or vertical, provided with agitating gear, holding a few tons each, heatable by a steam-jacket or steam-coil. After the solution has been effected, the liquor is cooled, with continuous agitation by running cold water through the jacket. The crystallized mass is removed from the mother liquor by a vacuum filter, and the last remainder of the pyridine mechanically kept back is removed in a steam-heated drying oven. Thus a greenish powder of distinctly crystalline appearance is obtained. From the mother liquor the pyridine is recovered by distillation. The residue left behind is an excellent material for the recovery of *carbazol* and *phenanthrene*, which up to the present are not saleable in quantity. This also holds good of *acenaphthene* and *fluorene*, which appear in the first runnings when distilling phenanthrene, and of *chrysene* and *pyrene*, which can be got from the residue in the distillation of the first anthracene oil, or by the distillation of pitch (p. 455).

It would appear from Kraemer and Spilker's description in *Muspratt-Bunte*, viii., 68, that this process is carried out on a large scale in the German tar-works, but according to a com-

munication from Dr Kraemer, they have never obtained chrysene (let alone pyrene) in this manner.

The Farbenfabriken vorm. Friedr. Bayer & Co. (Ger. P. No. 68474) employ liquid *sulphur dioxide*, which dissolves the impurities of crude anthracene, but very little of the anthracene itself. 600 kg. crude anthracene is mixed in a wrought-iron agitator with 2400 kg. SO_2, first exhausting the air and then allowing the liquid SO_2 to enter. The reaction having ceased, the mass is forced by its own vapour-pressure into an iron, steam-jacketed, filtering-tower, where anthracene of 70 or 80 per cent. remains behind. The mother liquid is distilled, the SO_2 being collected and recondensed by means of an air-compressor.

Another patent of the same firm (No. 78861) recommends *acetone* as purifying agent. 560 kg. crude anthracene is stirred in a steam-jacketed cylinder with 750 kg. acetone or an analogous substance, for an hour at 60° C. After cooling, the separated anthracene is filtered and washed with 375 kg. acetone. The second liquor is used over again, the first is distilled to recover the acetone. From crude anthracene of 34 or 35 per cent an article of 82 per cent. is easily made, and only a few per cent. of anthracene remains in the residue after distilling the acetone.

Wilton (B. P. 27559, 1898; Ger. P. 113291, abandoned in 1904) purifies rough anthracene by *liquid ammonia* (anhydrous), which dissolves out most of the impurities and leaves the anthracene behind.

The Aktien-Gesellschaft für Teer- und Erdöl-Industrie (Ger. P. 111359) purify crude anthracene in the following manner:—Most of the phenanthrene is removed by fusion and fractional crystallization; then carbazol is removed by treatment with 50 per cent. solution of caustic potash at not above 260°, and the remainder of the phenanthrene is eventually dissolved out by means of 90 per cent. benzol. Thus anthracene testing 90 per cent. is obtained as a brownish powder. This patent was abandoned in 1902.

Luyten & Blumer (Ger. P. 141186) treat drained, oily, rough anthracene without pressing, directly with a volatile solvent, filter, wash, and dry. They assert that thus purer anthracene is obtained than by the treatment of pressed anthracene, the mixture of the volatile solvent with the high-boiling oils which

accompany the anthracene being particularly adapted to the purification of the anthracene.

E. Wirth (Ger. P. 122822; Fr. P. 302998) suspends the crude anthracene in benzol and treats it with nitrous acid, which, under the conditions chosen, does not act on anthracene, but transforms carbazol, etc., into nitrosocarbazols, which are separated from the anthracene with the solvent. The nitrous acid is recovered from the nitrosocarbazol by means of sulphuric acid, thus obtaining a technically useful oxide of carbazol.

Vesely & Votocek (B. P. 27596, 1904; Ger. P. 164508) heat a solution of crude anthracene in a solvent immiscible with sulphuric acid, with concentrated sulphuric acid (which acts also upon carbazol), *e.g.*, 100 parts crude (35 per cent.) anthracene (containing 12·8 per cent. carbazol), 300 solvent naphtha, and 100 sulphuric acid. The heating is continued with agitation for a few minutes, the acid is drawn off, the solution is freed from acid by agitation with calcium carbonate, filtered, and allowed to crystallize. Thus anthracene of 84 per cent. is obtained, with only 1 per cent. carbazol, and by once recrystallizing from benzol it is brought to 95 per cent.

The Aktien-Gesellschaft für Anilinfabrikation in Berlin (Ger. P. 178764) fuses crude anthracene with caustic potash, and submits it to a distillation *in vacuo*, passing the distilling anthracene into solvents in which it is soluble at higher temperatures and allowing it to crystallize by cooling. Thus all commercial alizarines can be purified by a single operation; even where very much carbazol is present, 95 or 96 per cent. of the anthracene employed is obtained as an article of 95 to 98 per cent. real anthracene.

Scholvien's patents (Belg. P. 177419; Fr. P. 335013) are almost identical with the above-mentioned Ger. P. 111359.

The preparation of *chemically pure anthracene*, as described by Znatowicz,[1] by nascent hydrogen in an acid solution, is hardly of technical interest (*cf.* also p. 197).

The men who are employed in the purification of anthracene are sometimes afflicted by a special disease, similar to the "chlorine-ache."[2] As this disease only occurs through the

[1] *Chem. Zeit.*, 1900, 772.

[2] Russig, *Chemische Zeitschrift*, iv., 488; v., 315.

direct contact of the skin with the crude anthracene, it can be kept off by great cleanliness, and by employing as much machine-work as possible.

Subliming the Anthracene.

Before anthracene, purfied by any plan, can be converted into anthraquinone, it must undergo a suitable preparation (not

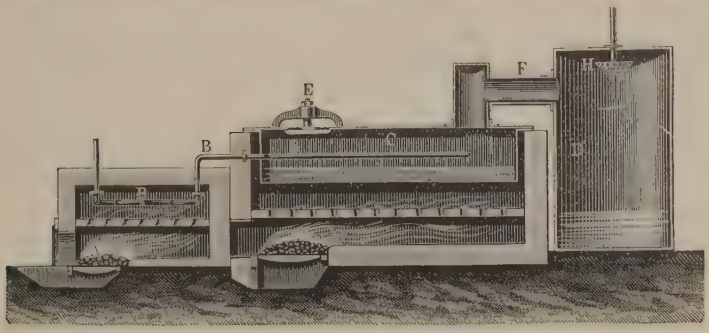


FIG. 142.

merely by grinding) to reduce it to a sufficiently fine powder to facilitate the action of the oxidizing agents. For this purpose it is usually *sublimed* and precipitated in an extremely fine

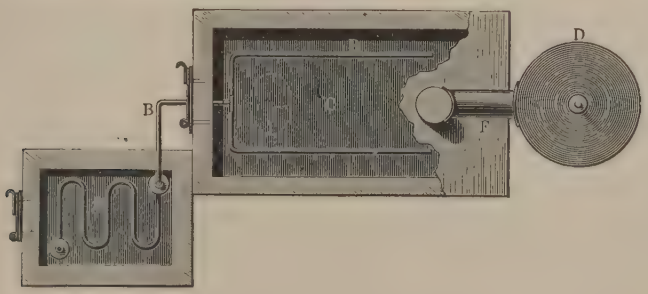


FIG. 143.

state of division by means of water. The sublimation is always effected by superheated steam, in an apparatus represented by Figs. 142 and 143[1] (or in a deeper still, fitted up in a similar

[1] From Wurtz, *Dictionnaire de Chemie*, Supplément, p. 65.

manner). The anthracene is placed in a shallow pan, C, made of boiler-plate and heated from below, so that the anthracene fuses and forms a layer an inch or two in depth. The steam arriving in the pipe B is heated by the flame of the fireplace A to 220° to 240°, and issues from the flattened tube B′ (which is perforated by many holes) to the melted anthracene, which it causes to sublime and carries away through the wide delivery-tube F into the brickwork or wooden chamber D. In this a jet of water, finely divided by the rose H, descends, condenses the steam, and suddenly precipitates the anthracene brought over in the finest state of division. The partial vacuum caused in this operation no doubt assists the sublimation in C. After draining, the anthracene, now a white mass of fine scales, can, after passing it through a sieve to separate any coarser particles carried along in the melted state, be oxidised while still wet. The loss in this operation amounts to 2 or 3 per cent. According to Wurtz, the strength of the anthracene is thereby raised from 50 to 60-65 per cent.; but this is evidently a mistake. According to Auerbach (*loc. cit.*, p. 11), the effect of the sublimation is not a purification at all, but only a mechanical division. At any rate the purification cannot exceed the loss above mentioned of 2 or 3 per cent.; and this has been confirmed by all the alizarin-makers I have consulted. Sometimes no fire is applied to the still from without; but then the steam must be superheated to at least 300° and blown into the mass itself. The residue left in the still, when being cautiously distilled over a naked fire, yields carbazol, phenylnaphthyl carbazol, pyrene, and especially chrysene.

E. Perret (Wurtz, *loc. cit.*) proposes heating the anthracene to 250° and driving the vapour, mixed with air or carbon dioxide, by means of a fan-blast into chambers to be condensed in the dry way. A similar proposal was made by Schuller[1]; but it does not seem so rational as the wet condensation.

Anthracene obtained synthetically.

Bradley & Jacobs (Ger. Ps. 125036 and 142051) obtain anthracene, together with benzene and naphthalene, by heating barium carbide with caustic baryta and soda to 600° to 1200° C.

[1] *Berl. Ber.*, 1870, p. 548.

Thereby the hydrocarbons are obtained according to this equation (for benzene):

$$3BaC_2 + 3Ba(OH)_2 = C_6H_6 + 6BaO.$$

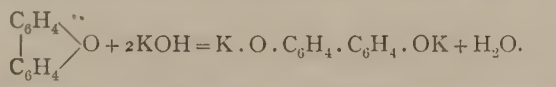
At present there is no chance of carrying out this reaction in a profitable way. Their patents were abandoned in 1904.

Preparation of Phenanthrene, Fluorene, and Carbazol, as by-products.

Kraemer and his co-operator, Weissgerber, have succeeded in preparing the hydrocarbons contained in the heavy tar-oils, boiling rather lower than anthracene, in the first instance phenanthrene and fluorene, by the action of fusing caustic potash on the respective tar-oils or by-products from the purification of anthracene. Patents for this have been taken out by the Aktien-Gesellschaft für Teer- und Erdöl-Industrie, Berlin (B. P. 5047, 1901; Ger. Ps. 124150 and 130679). Fluorene, similarly to carbazol (*cf.* p. 240), on being fused with caustic potash at 280° C., yields a solid potassium compound:

$$C_{13}H_{10} + KOH = C_{13}H_9K + H_2O.$$

According to the first German patent (124150), the fluorene is split off again from its potassium compound by treatment with water, after having previously removed the unattacked hydrocarbon floating on the potassic melt. This patent was not renewed after the first few years. According to the second patent (130679), the alkaline melt contains also diphenol-potassium, formed from the diphenylene oxide (p. 224):



It is not even necessary to remove the hydrocarbons floating on the top, but merely to treat the melt with water, which takes up the potassium compounds of diphenol and its homologues, from which the latter can be recovered; the diphenol can be recovered by any acid, even CO_2. After the solid deposits from the high-boiling fractions of coal-tar have been well fractionated the corresponding hydrocarbons may be immediately obtained in a pure form by means of this process, provided that these oils had been previously freed from acids and bases

in the usual manner, and that the neutral liquid constituents had also been removed by combined pressure and heat.

Concerning the recovery of carbazol and phenanthrene from the pyridine solution in the process described on p. 493, we refer to that place.

The carbazol obtained by this and other purifying processes (*cf.* p. 495) is not easy to dispose of. The Chem. Fabr. Akt.-Ges. in Hamburg (Ger. P. 81237) proposes to heat it in a pan gradually up to a bright red heat; carbon is separated and cyanide of potassium is formed, small proportions of carbazol, ammonia, etc., being removed by volatilization. The yield is increased by adding potash, soda, or similar substances during the fusion; and ferrocyanide can be obtained by the addition of iron.

Crude phenanthrene is used by Dreher (Ger. P. 118233; *Z. angew. Chem.*, 1901, 324) for preparing a rosin soap containing much free rosin for sizing paper. It is also used in the treatment of camphor, in lieu of naphthalene, for the manufacture of celluloid, as it does not possess the strong smell of naphthalene and does not evaporate so quickly.

Sulphonic acids of phenanthrene are used for making cresols soluble in water (Ger. P. 128880, Akt.-Ges. f. Teer- u. Erdöl-Industrie; B. P. 7119, 1901).

The literature on phenanthrene up to a few years ago is fully treated by M. A. Kunz in a special book: *Untersuchungen über Phenanthren* (Berlin, Julius Springer, 1902).

We lastly quote a number of recently published investigations on the companions of anthracene which hitherto possess only scientific interest; viz., the work of Thiele and his co-operators (*Ber.*, 1900, 851); Boes (*Pharm. Zeit.*, 1901, 915; *Chem. Zeit. Rep.*, 1901, 315, 364); Moschner (*Ber.*, 1900, 757); Kraemer and Spilker (*Ber.*, 1900, 2263); Loeb (*Ber.*, 1901, 915); Bone and Jordan (*Chem. Zeit.*, 1901, 591); Dimroth (*Pharm. Zeit.*, 1901, 352), and many others in the following years.

Fluorene is prepared by the Gesellschaft für Teerverwertung Duisburg-Meiderich (Ger. P. 203312) by transforming the raw material into an alkaline compound which can be separated from the unchanged hydrocarbons. This compound is prepared by heating the material with sodium, or sodium amides, or sodium in the presence of ammonia, to temperatures between 110° and

250° C.; 300 parts of the mixture of hydrocarbons is heated during two hours with 20 parts of sodium, with agitation, to 150° to 200°. After cooling, the supernatant layer of unchanged hydrocarbons is mechanically separated from the fluorene compound remaining at the bottom. The latter is crushed and put into water, whereby fluorene is produced in the state of powder. It contains a small quantity of a high-boiling condensation-product, formed in the fusing process from the fluorene, from which it is separated by distillation *in vacuo*. When employing sodium amide, the reaction goes on at a lower temperature; it is sufficient to heat during an hour to 100° and another hour to 150° C.

Yields and Statistics.

The yield of anthracene varies both with the quality of the tar and with the care bestowed upon extracting it. While Scotch tar yields little or no anthracene, the German and Dutch works obtain from 0·3 to 0·35, at most 0·45, parts of pure anthracene (Luck's test) from 100 parts by weight of tar. In England the yield is much more considerable: North-Country tar, on the average, yields 0·5; London tar from 0·8 to 0·9 per cent. by weight of pure anthracene. From a communication by Mr J. Leahy, Thurston Chemical Works, Sittingbourne, it appears that the average yield of anthracene at that works for over 18 months has been equal to 0·676 per cent. pure anthracene on the coal-tar distilled.

H. Elliott[1] states the yield of anthracene from water-gas tar as 2·63 per cent. [but that is hardly possible!].

Compare also the statements in Chapter V., pp. 409 *et seq.*

W. H. Perkin,[2] in 1885, estimated the yearly production of anthracene in the United Kingdom at about 6000 tons, 30 per cent., or nearly 2000 tons pure anthracene, which is largely in excess of the present requirements of the manufacture of alizarin. This seems to make it a hopeless undertaking to manufacture anthracene by distilling pitch (*cf.* pp. 454 *et seq.*), or by superheating petroleum residues and the like (pp. 141 *et seq.*), or by distilling rosin with alkali, as patented by R. Irvine (B. P. 4276, 1882).

[1] *Amer. Chem. Journ.*, vi., p. 248 (1884).
[2] *J. Soc. Chem. Ind.*, 1885, p. 433.

Anthracene is principally consumed in the German alizarin-works, which, according to reliable statistics, in 1880 worked up 1400 tons of *pure* anthracene, 200 tons of which were supplied by German tar-distillers, the remainder mostly by English distillers. Since then much more anthracene has been consumed, but the production has equally increased, in Germany mainly through the strong development of the coke-tar industry (pp. 58 *et seq.*). This is proved by the following table of the importation of anthracene into Germany (the quantity of anthracene exported from that country is quite insignificant).

Year.	Anthracene imported.	Value.	Year.	Anthracene imported.	Value.
	Tons.	Thousands of Marks.		Tons.	Thousands of Marks.
1892 . .	5981	4785	1899 . .	4365	1746
1893 . .	5523	4419	1900 . .	3894	1168
1894 . .	3299	2639	1901 . .	3293	823
1895 . .	5913	5321	1902 . .	2876	590
1896 . .	6305	4729	1903 . .	2048	236
1897 . .	6490	3245	1904 . .	1230	172
1898 . .	8027	3211			

In the year 1907 Germany imported and exported :—

	Tons.	Tons.
Anthracene . . .	2418	32
Heavy coal-tar hydrocarbons—(anthracene, carbolic oil, etc.)	7034	50,802

Two qualities of anthracene are quoted in the market. *A* contains 40 to 45 per cent., *B* 25 to 40 per cent. pure anthracene. The former is obtained principally from Newcastle coals, and contains less paraffin and other troublesome impurities than *B* quality, which is made from Lancashire and Yorkshire coal, with much cannel-coal. The "unit" of trade means $\frac{1}{100}$ cwt. = 508 g. *pure* anthracene.

The fluctuations in the price of anthracene are enormous. Perkin (*loc. cit.*) paid per lb. in 1870-1871 1s. 6d., in 1872, 1s. 6d. to 5s. and even 5s. 6d. The value in 1881 was about 3s., in 1886 about 9d.; in July 1887 in was 1s. 3d.; in August 1899 the London price for the unit of quality *A* (30 per cent.) was only 4d.

In 1900 (*J. Amer. Chem. Soc.*, xxii., No. 9), Tayne states the manufacture of anthracene (40 per cent.) from coal-tar had been abandoned for some years in the United States, because its

price was so low that it did not pay to make it, as previously, for exportation to Europe.

Russig, in *Chem. Zeit.*, 1901, I., No. 2, shows the decline of prices of anthracene from $3\frac{1}{2}$ marks per unit in 1890 to 0·4 mark in 1901 by a very instructive diagram.

Properties and Analysis of Anthracene.

The properties of *pure* anthracene have been described, pp. 198 *et seq.*

Rough anthracene, before sublimation, is a brownish-green friable mass, still containing most of the substances mentioned on pp. 198 *et seq.*

Zeidler[1] has made an extensive investigation of crude anthracene, and has found the following substances:—

I. Insoluble in acetic ether: anthracene, chrysene, and other bodies not yet examined.

II. Soluble in acetic ether.

A. Soluble in cold 40 per cent. alcohol.

1. Insoluble in carbon disulphide: carbazol.
2. Soluble in carbon disulphide: phenanthrene, fluorene, hydrocarbons melting at 92°·5.

B. Soluble in moderately warm benzene: synanthrene, hydrocarbons melting at 97° and 104°.

C. Soluble in hot benzene: anthracene, pseudophenanthrene.

D. Insoluble in hot benzene: carbazol.

Methyl-anthracene is not mentioned here, although it occurs largely in some descriptions of crude anthracene.

It is not a very easy task to distinguish the different substances occurring in crude anthracene; and we cannot here go into this matter, which does not interest the tar-distiller so much as the alizarin-maker and the scientific chemist. We will only mention that the identification of the different hydrocarbons is often promoted by the characteristic combinations they form with picric acid. Watson Smith[2] has proposed to employ the fused chlorides of antimony and bismuth for discriminating the solid hydrocarbons.

Considering the high value of anthracene, and the extremely

[1] *Ann. Chem. Pharm.*, vol. cxci., p. 285.

[2] *Chem. News*, xl., p. 26.

varying percentage of pure anthracene in the rough product, it is evidently of the greatest importance to possess a reliable method of analysis. Formerly this was merely attempted by the action of solvents for the impurities, which, however, is so imperfect that those methods have been almost entirely replaced by Luck's method, which certainly requires some manipulative skill. But as the old methods are not yet altogether obsolete, we must here describe them.

These methods were intended to remove the foreign matters and to leave pure anthracene behind. Evidently this cannot be done with any approach to exactness; for, on the one hand, the impurities are not entirely soluble (some are even less so than anthracene itself) in the liquids employed; on the other hand, the latter dissolve sensible quantities of anthracene as well. Hence different solvents yield quite discordant results; but, apart from the evident impossibility of thus ascertaining the true percentage of pure anthracene, each method by itself gives pretty constant results, on the condition of strictly keeping to the same mode of manipulation, which must be agreed upon between buyer and seller. In the sale-note the solvent employed must be specified (*e.g.*, whether carbon bisulphide or alcohol), its quantity, its specific gravity in the case of alcohol, and the exact way of manipulating it stated. Thus, if the product be of an oily nature, a higher value will be found if the sample be pressed before analysing it, because the oils augment the solvent power of the liquid employed for anthracene itself.

To begin with, a proper *sampling* is very important. A 1½-inch hole is bored in both ends of each cask, and a 2-foot steel tube, with wooden handle, cut open lengthways with sharp edges, is twisted into the cask from both ends right into the centre. The boring cores thus obtained are ground up and well mixed, and a reduced sample taken therefrom

The following are the methods employed in practice:—

1. *Alcohol Test* (*Spirit Test*).—Triturate the sample well in a mortar; weigh out 20 g., which stir well up in a beaker with 150 g. of alcohol of the strength stipulated in the sale-note (usually sp. gr. 0·825); cover the beaker with a watch-glass, gradually heat to boiling, and then cool by placing it in water of 15·5. After an hour the liquid is decanted through a filter,

and the undissolved part is gradually washed with alcohol of the same strength as before, and at the temperature of 15°·5, till the filtrate and washings together amount to 400 c.c. If sand is clearly perceptible at the bottom of the beaker, it is kept back; the remainder is placed in a weighing-glass, dried at 100° in a water-bath, and weighed. Its weight multiplied by 5 is accepted as the percentage of anthracene.

According to Auerbach's *Anthracen*, 20 g. of anthracene cake are heated with 100 c.c. of alcohol of 98 per cent., and the washing continued to a bulk of 300 c.c.

In order to test the so-called pure anthracene of this operation for foreign insoluble bodies, sometimes 5 g. are boiled with as much alcohol as suffices to dissolve all the anthracene, and the liquid is filtered while hot. The residue is washed with boiling alcohol; and the residue insoluble in this liquid is deducted from the percentage found above; if its weight amounts to more than 1 per cent., it must be considered an adulteration.

In any case the melting-point of the so-called anthracene is determined. It is put into a finely drawn-out glass tube, in which it should occupy a space of about an inch in length; the tube is fastened by means of a small piece of elastic tubing to a good thermometer; and both are immersed in a paraffin bath, which is slowly heated. The point at which the first drop runs down is taken as the melting-point. After the mass has completely liquefied, the lamp is removed and the temperature at which solidification again takes place is observed. The mean between this and the point found above is the *mean melting-point;* it ought not to be below 190.°

Sometimes the following course is taken:—190° (or some other temperature) is accepted as the standard melting-point; and it is ascertained how much substance having this melting-point is obtained by employing an indefinite quantity of alcohol, but always of the same specific gravity (say 0·825). A sample is treated as above, and the melting-point ascertained. If this be 190°, nothing further is requisite; but if above that, a new test is made with less alcohol; if below, with more alcohol. If, say, sample No. 1 has been boiled with 150 c.c. alcohol and washed to 400 c.c., and has then yielded 40 per cent. melting at 195°, sample No. 2 is boiled with only 100 c.c. alcohol and

washed to 300 c.c.; this yields more, say 49 per cent., melting at 188°. The quantity melting at 190° is then found by the proportion:—

$$195-188 : 49-40 = 195-190 : x,$$

where x is the amount to be added to the lower percentage. On carrying out the calculation we get

$$x = \frac{9 \times 5}{7} = 6{\cdot}4;$$

hence the sample contains $40+6{\cdot}4=46{\cdot}4$ substance melting at 190°.

The spirit test is wrong in principle; for alcohol dissolves some anthracene and does not remove the chrysene. These two opposite errors may accidentally compensate each other, but certainly not in most cases; and this method is therefore undoubtedly inaccurate.

2. *Bisulphide of Carbon Test.*—Ten grammes of the well-mixed sample are shaken in a stoppered bottle with 30 c.c. carbon bisulphide, and allowed to stand an hour at 15°·5. The undissolved matter is thrown on a filter, the bottle is washed out with 30 c.c. of carbon bisulphide; but any sand is left behind. After the liquid has run through, the filter is pressed gently, but quickly, first with the fingers and then between blotting-paper in a strong press. The insoluble matter is put on a watch-glass dried for an hour at 100°, and weighed; its weight, multiplied by ten, indicates the percentage. The "mean" melting-point of the substance ought not to exceed 212° to 214°.

Déhaynin heats 20 g. of anthracene with 40 c.c. of carbon bisulphide for 20 minutes, with constant stirring, cools down to 15°, filters through a tared filter, and washes with so much carbon bisulphide that the total amounts to 100 c.c. The residue is dried, weighed, and taken as pure anthracene.

Perkin grinds up 50 g. of anthracene with 10 fluid-ounces of petroleum spirit of sp. gr. 0·740, passes through canvas, and washes the vessel and the residue with another 20 fluid ounces. The filter is squeezed out, first by hand, then in a vice. The residue is powdered, put into a bottle holding 6 or 7 oz., and vigorously shaken up for 2 or 3 minutes with 5 oz. of carbon bisulphide. It is then placed upon a tared filter, pressed between

blotting-paper, dried, and weighed. The product ought to show a mean melting-point of not below 200°, nor above 212°.

The bisulphide of carbon test, or the same combined with the application of petroleum spirit, has remained in use for a long time, although it is perhaps even worse than the spirit test. Chrysene is very little soluble in carbon bisulphide; hence by this process a product may be obtained which shows the proper melting-point and yet is not anthracene. Besides, carbon bisulphide dissolves 2 per cent. of anthracene; and, owing to its quick evaporation, very discordant results will be obtained by different chemists, according to the difference of manipulation, the deviations extending to 4 or even to 6 per cent.; 2 or 3 per cent. is quite usual here, as well as with the spirit test.

A comparison between the results of the spirit and bisulphide of carbon tests shows that the two do not bear a constant proportion to each other. In the case of low products the alcohol test indicates four times as much as the carbon-bisulphide test; with higher percentages the discrepancy becomes gradually less, the alcohol test uniformly giving a much higher result; only at the highest percentages does the inverse ratio take place. There are also considerable differences between the melting-points. This is proved by a table given by Versmann as the result of 30 duplicate tests according to both methods, which need not be repeated here.

3. *Anthraquinone Test.*—Anthraquinone, the product of the oxidation of anthracene, obtained in the manufacture of alizarin, appears in the pure state as a mass of pale yellow needles, when precipitated from solutions, but in the shape of long, thin, golden-yellow needles when sublimed. It fuses at 277° and boils considerably above the boiling-point of mercury, but it sublimes very much below that. It is insoluble in dilute acids or alkalis, and is not even affected by hot concentrated hydrochloric acid or solution of caustic alkalis; but it dissolves unchanged in concentrated sulphuric acid at 100°, and is again separated by dilution. It is very little soluble in alcohol and ether, but more so in hot benzene.

It had been previously recognised that the oxidation of crude anthracene to anthraquinone, and the estimation of the latter, is the only reliable method of analysis in this case. But

the merit of investigating all the points necessary to elaborate a system of testing belongs to E. Luck, whose name is justly attached to this test. Luck had first to ascertain whether a weighed quantity of rough anthracene, on oxidation with glacial acetic acid and chromic acid, yields the theoretic quantity of anthraquinone, whether the latter is not oxidized further by long contact with chromic acid, and what is the behaviour of the regular (accidental or purposely added) companions of anthracene during the chromic-acid treatment. Luck's results were as follows:—

I. Pure anthracene, dissolved in glacial acetic acid, and treated at boiling-heat with 3 to 4 parts of chromic acid, yields 99·4 per cent. of the theoretically calculated quantity of anthraquinone.

II. Pure anthraquinone, dissolved as above and boiled with 3 to 4 parts of chromic acid for two hours, on dilution with water yielded the original quantity of the anthraquinone employed (employed 0·447, recovered 0·446 g.).—But more recent experiments refute this statement: by successive treatment of anthraquinone with constantly renewed quantities of glacial acetic acid and chromic acid, 1 g. of 93·2 per cent. anthraquinone was reduced to 0·576 g. Hence anthraquinone does not resist the oxidizing action of chromic acid to the extent assumed by Luck.

III. The substances accompanying or contaminating anthraquinone are, by a sufficiently prolonged chromic-acid treatment, completely converted into bodies soluble in acids or alkalis, and can thus be separated from it. This holds good of phenanthrene, chrysene, paraffin, bitumen, etc.

Luck's method in its original shape was as follows:—

One gramme of the rough anthracene is dissolved in a small flask with 45 c.c. of boiling glacial acetic acid.[1] If required, the solution is filtered quite hot through a small filter, and a solution of 10 g. chromic acid in 5 c.c. of water and 5 c.c. of glacial acetic acid is added in small quantities, so that the liquid remains constantly boiling. The chromic-acid solution is run in, until a distinct and permanent greenish-yellow colour appears, or till after prolonged boiling a drop of the solution, put on a

[1] Basset (*Chem. News*, lxxix., 157) draws attention to the fact that a bad quality of acetic acid may produce errors by reducing chromic acid.

bright silver coin, produces after a few minutes a reddish spot of silver chromate. The liquid is now allowed to cool, is gradually diluted with 150 c.c. of water, and filtered after a few hours; the anthraquinone remaining on the filter is washed, first with water, then with hot, very dilute solution of caustic potash, then again with water, and dried at 100°. After weighing, the anthraquinone is quickly removed from the filter, the latter is weighed, and its weight is deducted from the original gross weight. To the net weight thus obtained an addition of 0·01 g. is made, because, if according to the above prescription 50 c.c. of glacial acetic acid and 150 c.c. of water have been employed, 10 mg. remain dissolved in the filtrate.—Commercial chromic acid often contains lead; in this case the anthraquinone, after washing with water and alkali, must be treated with a hot solution of ammonium acetate.

It was soon found that even in this way no perfectly accurate results were obtained. A portion of the impurities is not completely oxidized, and is thus estimated as anthraquinone. Hence Luck subsequently prescribed treating the latter with an alkaline solution of potassium permanganate. The anthraquinone, after washing with alkali, is washed into a small beaker or dish, is rendered faintly alkaline, heated to boiling, and a solution of potassium permanganate is gradually added, till it is no longer reducible and the green colour is changed into pale pink. Now a little oxalic acid and sulphuric acid are added, to reduce the excess of potassium permanganate and to dissolve the manganese dioxide formed. The whole is now filtered. Upon the same filter the precipitate is washed to perfect neutrality, then with dilute solution of sodium carbonate, then again with water, dried at 100°, and weighed. Luck states that usually 10 g. of chromic acid are quite sufficient, but exceptionally 15 g. may be required for perfect oxidation. Auerbach (*loc. cit.*) states that this indefiniteness sometimes produces awkward results. Thus a sample of rough anthracene in four tests with 10 g. of chromic acid regularly yielded 26 per cent., but in six tests with 15 g. of chromic acid it produced only 23 per cent., although in both cases an excess of chromic acid was present. Probably a small excess of chromic acid in the presence of chromium acetate does not oxidize anthracene any further; this requires a larger excess. It would

therefore be best to prescribe in all anthracene-contracts 15 g. of chromic acid for 1 g. of rough anthracene, which seems to be sufficient in every case. The time allowed for the oxidation has no influence; three or four hours suffice, and six or eight hours do not alter the result.

An objection to Luck's method is the hot filtration which is prescribed as sometimes necessary. Organic bodies are anyhow destroyed during the oxidation; inorganic ones, which are mostly non-volatile, as sand, are best estimated by igniting a sample of crude anthracene. But if the substances insoluble in glacial acetic acid are to be estimated, it is in any case much safer to extract a weighed sample of crude anthracene completely, than to filter the mixture intended for analysis whilst hot, in which operation a portion of the anthracene is lost by evaporation of the acetic acid and crystallization on the filter.

J. T. Brown[1] proposes making the analyses more correct by taking a larger average sample, and by other precautions. He weighs off 50 g. of crude anthracene, and at the same time measures off 250 c.c. of petroleum spirit. With a portion of the latter he triturates the anthracene in a mortar so as to form a thin cream, pours it into a weighed filter (taking care to leave in the mortar any grit or sand that may be present), and employs the rest of the petroleum spirit in rinsing out the mortar and washing the precipitate on the filter. After draining, fold carefully, press between blotting-paper, dry at from 60° to 80°, and weigh. Crush the contents of the filter to fine powder, and weigh out the gramme required for the anthraquinone test.—This proposal is useless; for the temperature, the specific gravity of the petroleum spirit, etc., will greatly influence the result.

It is a further objection to Luck's method that even after treating with permanganate the anthraquinone is still impure, If pure it would dissolve without change in sulphuric acid, and would only at a temperature above 200° be converted into a sulphonic acid. But Luck's quinone when treated with concentrated sulphuric acid turns blue or brown, which proves the presence of foreign bodies; even if the acid remains colourless. a coloured solution is obtained by subsequently boiling the quinone with dilute solution of caustic soda. Hence the results

[1] *Chem. News*, xxxiv., p. 136.

of purifying by permanganate vary from those of the purification with sulphuric acid (to be subsequently described) to the extent of from 1 to 8 per cent.

For this reason Meister, Lucius, and Brüning[1] have proposed the following method of analysis, which is now well-nigh universally adopted, and is sometimes called the "Höchst test." Take 1 g. of anthracene, put it into a flask with condenser of 500 c.c. capacity, add to it 45 c.c. of glacial acetic acid, and heat to ebullition. To this solution, which is kept boiling, add drop by drop a solution of 15 g. of chromic acid in 10 c.c. of glacial acetic acid and 10 c.c. of water. The addition of the chromic solution should occupy two hours, after which the liquid is kept boiling for two hours longer. The flask with its contents is to stand twelve hours, then to be mixed with 400 c.c. of cold water, and again kept standing for another three hours. The precipitated anthraquinone is now collected on a filter and washed, first with pure water, then with 200 c.c. of boiling dilute alkaline solution (1 KOH in 1000 water), and finally with pure water hot. The quinone is now washed from the filter into a dish and dried at 100° C.; it is then mixed in the same dish with 10 c.c. of fuming sulphuric acid of 68° Baumé (sp. gr. 1·88) and heated to 100° C. for ten minutes on a water-bath. The acid should be pure and limpid and contain about 16 per cent. SO_3 in the free state. The quinone solution thus obtained is poured into a flat dish and kept for twelve hours in a damp place (say, on a thick layer of blotting-paper, a glass jar being placed over it all) to absorb water; then add 200 c.c. of cold water to the contents of the dish, collect the precipitated quinone on a filter, and wash first with pure water, then with boiling alkaline solution, and finally with pure water hot. The anthraquinone is now placed in a platinum dish, dried at 100°, and weighed. After volatilizing the quinone by heating the dish, the latter is weighed with the particles of coal and the ash. The difference between the two weights gives the weight of the anthraquinone obtained; and it is to be calculated in the usual manner into anthracene (multiplication by coefficient 0·8558). A correction for the quinone dissolved in the acetic acid is, under the conditions here prescribed, not necessary or admissible.

The Table on page 312 will save a calculation.

[1] *Z. anal. Chem.*, p. 61.

According to the investigations of F. H. Davis and Lucas,[1] the result of Luck's test does not at all agree with that of the carbon-bisulphide test; the latter mostly shows a great deal too much. But in one case Davis obtained from the same sample by the alcohol test (sp. gr. 0·825) 34·645 per cent., melting-point 187·5; by carbon-bisulphide 23·250, melting-point 198·2; by Luck's test, 28·358. Lucas found by the carbon-bisulphide test in three cases 0·4 to 2·7 per cent. too little, in seventeen cases 2·5 to 23·78 per cent. too much. He confirmed Luck's opinion that all the substances accompanying anthracene are by the chromic-acid treatment converted into bodies soluble in dilute alkali.

Quinone.	Anthracene.	Quinone.	Anthracene.	Quinone.	Anthracene.	Quinone.	Anthracene.
1	0·86	26	22·26	51	43·65	76	65·05
2	1·71	27	23·11	52	44·50	77	65·90
3	2·56	28	23·98	53	45·35	78	66·77
4	3·42	29	24·83	54	46·21	79	67·62
5	4·28	30	25·67	55	47·07	80	68·46
6	5·14	31	26·53	56	47·93	81	69·32
7	5·99	32	27·38	57	48·78	82	70·17
8	6·86	33	28·23	58	49·65	83	71·02
9	7·71	34	29·09	59	50·50	84	71·88
10	8·56	35	29·95	60	51·35	85	72·74
11	9·42	36	30·81	61	52·21	86	73·60
12	10·27	37	31·66	62	53·06	87	74·45
13	11·16	38	32·53	63	53·91	88	75·32
14	11·98	39	33·38	64	54·77	89	76·17
15	12·84	40	34·23	65	55·63	90	77·02
16	13·70	41	35·09	66	56·49	91	77·88
17	14·55	42	35·94	67	57·34	92	78·73
18	15·42	43	36·79	68	58·21	93	79·58
19	16·27	44	37·65	69	59·06	94	80·44
20	17·12	45	38·51	70	59·91	95	81·30
21	17·98	46	39·37	71	60·77	96	82·16
22	18·83	47	40·22	72	61·62	97	83·01
23	19·68	48	41·09	73	62·47	98	83·87
24	20·54	49	41·94	74	63·33	99	84·73
25	21·40	50	42·79	75	64·19	100	85·58

G. Schultz[2] holds that in one respect Luck's test gives too unfavourable a result, since chromic acid converts methylanthracene into soluble anthraquinone-carbonic acid and thus removes it, whilst during actual manufacture methylanthracene is converted into a quinone, and this into methylalizarin, which

[1] *Chem. News*, xxix., p. 169; xxx., p. 190; xxxi., p. 209.

[2] *Ber.*, 1877, p. 1051.

is said to have as much tinctorial power as alizarin. This, however, is not so; the products formed from methylanthracene impart to the alizarin colours a very objectionable shade, and hence alizarin-makers dread methylanthracene almost as much as paraffin (*cf.* Römer and Link, *Ber.*, 1883, p. 695). It occurs, however, in large quantities only in the anthracene recovered from the washing-naphtha (p. 481).

Holland[1] objects to Meister, Lucius, and Brüning's process (the "Höchst test"):—1st, that the 55 c.c. of glacial acetic acid, diluted though it be with 400 c.c. of water, still retains anthraquinone in solution, viz., on an average 0·0023 g.; 2nd, that boiling water dissolves some quinone, viz. 500 c.c. of water, 0·0019 quinone; 3rd, that in thrice washing the quinone from the filter a small loss is inevitable, which he estimates at 0·0020 g.; even with the most careful manipulation the total loss amounts to 0·0065 quinone = 0·0055 anthracene, and this quantity should always be added to that found. (According to information received by me from a most reliable authority, Holland's corrections are inadmissible, as the anthraquinone obtained by the "Höchst test" is itself not quite pure, but contains methylanthraquinone, anthraquinone-carbonic acid, and paraffin, which may cause an error of 1 per cent. and upwards in the opposite direction to Holland's corrections.)

Schwarz[2] believes the best test for crude anthracene to consist in washing it with a cold saturated solution of anthracene in glacial acetic acid. This test is not in use anywhere.

Anthraquinone, as obtained by the Höchst test, ought to be crystallized and of pale yellow colour. An orange or red colour indicates the presence of other quinones, especially those of phenanthrene and chrysene. The latter is also recognized by the production of an indigo-blue coloration on adding the sulphuric acid. In the case of impure anthraquinone, both the acid filtrate and the alkaline washings are deeply coloured. The above-mentioned quinones do not prevent the crystallization of anthraquinone, but this is done by the quinone, $C_{16}H_9NO_2$, produced by the oxidation of the imido-phenylnaphthyl (see below), which is one of the sources of the so-called "amorphous particles." This impurity can be destroyed by a somewhat

[1] Printed circular, dated Manchester, February 1879.

[2] *Wagner's Jahresber.*, 1877, p. 921.

longer-continued heating with sulphuric acid, which ought hence never to be omitted when crude anthraquinones of suspicious appearance have been obtained (Allen, *Commercial Organic Analysis*, 2nd ed., ii., p. 532).

Basset[1] proposes boiling the quinone, obtained according to Luck's method, for some time with a solution of chromic and nitric acid; pure anthraquinone does not lose weight, but that obtained from commercial anthracene loses 1 or 2 per cent. or more. Later on[2] he pointed out the fact that acetic acid sometimes reacts on chromic acid, which might be a source of error. Pure glacial acetic acid (16°·7 fusing-point) reduces in the cold 0·16 g. chromic acid (out of 15 g.) in twenty-four days, and 4·44 g. on boiling four hours under the same conditions as in Luck's test; less pure glacial acetic acid (13°·3 fusing-point) reduces under the same conditions 0·87 g. chromic acid in the cold, or 6·45 g. on boiling. These lower grades of acetic acid cause "high" results, by reducing the strength of the chromic-acid solution on keeping.

A. G. Perkin[3] points out that nothing certain is known as to the nature of the impurities destroyed by the action of fuming oil of vitriol on anthraquinone. They are probably chromium compounds of the carbon-acids or phenols formed during the oxidation, and decomposed only by heating with oil of vitriol. The quality B of crude anthracene, which requires special processes to yield good alizarin, is recognized by the presence of felt-like masses, the nature of which is not clearly known; it frequently contains β-methylanthracene, and in doubtful cases should be tested by converting it into alizarin.

Imido-phenylnaphthyl, which impedes the purification of the anthraquinone, can, according to B. Nickels,[4] be discovered by dissolving the sample of crude anthracene in hot benzene, filtering through a dry filter, and examining the solution with a spectroscope. The above substance produces a highly characteristic absorption-spectrum, showing two broad and well-defined black bands between the F and G lines, and another slightly more refrangible than G.

Paraffin (the objectionable presence of which in some

[1] *Chem. News*, lxxiii., p. 73. [2] *Ibid.*, lxxix., p. 157.
[3] *J. Soc. Dyers and Col.*, April 1897; *Chem. Centr.*, 1897, ii., p. 447.
[4] *Chem. News*, xl., p. 270, xli., pp. 52, 95, 117.

samples of anthracene has been mentioned on p. 490) can be detected and determined in the following manner:—Ten grammes of the sample is heated with 200 g. of strong sulphuric acid in a water-bath for about ten minutes, or until the anthracene is completely dissolved. Any considerable quantity of paraffin will rise to the surface in the form of oily globules. The solution obtained is cautiously poured into 500 c.c. of water contained in a tall beaker. After being thoroughly stirred, the liquid is allowed to cool, when any paraffin will rise to the surface, and having solidified, can be removed, washed with a little cold water, dried between blotting-paper and weighed. From 2 to 5 per cent. is the quantity usually present in Scotch anthracenes (Allen, *Commercial Organic Analysis*, 2nd ed., ii., p. 529). *Cf.* also p. 519.

Heusler and Herde[1] estimate the paraffin by placing at least 2 g. of crude anthracene into a flask holding 150 c.c., and adding, at first drop by drop, and cooling with ice-water, 25 c.c. fuming nitric acid. When all the acid has been added, the whole is digested until the anthracene is dissolved, then heated on the water-bath till all the paraffin is melted. The latter after cooling is collected on a small filter and mixed with fuming nitric acid, until the filtrate does not become opaque on the addition of water. Then the washing is continued with water, until the acid reaction has ceased. Now a test-tube is placed under the filter and the paraffin is washed into this, first with alcohol, then with warm ether. The alcoholic solution is evaporated in a small porcelain dish on the water-bath; afterwards the ethereal solution is added and is also evaporated; the paraffin is dried for half an hour at 105° or 110°, and weighed.

Kraemer and Spilker (in *Muspratt-Bunte*, viii., 70) recommend the following method as very accurate:—Shake 10 g. of the very finely-ground anthracene in a 100 c.c. flask with 70 c.c. ether for ten minutes, fill with ether up to the 100 c.c. mark, mix, and put aside for settling. Put 50 c.c. of the clear solution into a porcelain dish, allow the ether to evaporate, and dry the residue at 100° for half an hour. After cooling, triturate it finely, add 8 c.c. fuming sulphuric acid (with 20 per cent anhydride), mix well, cover the dish with a watch glass, and

[1] *Z. angew. Chem.*, 1895, p. 253.

heat for three hours at 100° C., frequently stirring. Wash the contents of the dish, by means of 500 c.c. hot water, into a beaker, and after cooling, pass through a dry filter and wash this and the beaker with cold water until barium chloride does not produce a cloud in the filtrate. Allow the filter to drain thoroughly, moisten it with absolute alcohol, and wash the paraffin by means of ether into a weighed dish until a few drops of the running-off ether do not leave any residue on evaporation. Remove also the last traces of paraffin from the beaker by means of ether. Evaporate the ethereal solution in a moderately hot place, dry the residue at 105° C. for half an hour, and weigh it as pure paraffin.

The following process for estimating small quantities of paraffin in anthracene is recommended in *The Oil and Colourman's Journal*, 1906, p. 487 (*Z. angew. Chem.*, 1907, p. 463). Heat 10 g. of the anthracene with 108 g. concentrated sulphuric acid in a beaker on the water-bath till dissolved, and after cooling pour into 400 c.c. cold water. Extract the solution by shaking it twice with petroleum spirit; mix the extract first with half its volume of 5 per cent. caustic soda solution, then four times with one-eighth of its volume of cold concentrated sulphuric acid, and lastly, remove the acid by washing with water. Now distil the residue from a tared flask; the residue, multiplied by 10, indicates the percentage of paraffin.

Small quantities of *paraffin* can be detected in anthracene by the following method (*Z. angew. Chem.*, 1907, 463):—Heat 10 g. with 108 c.c. concentrated sulphuric acid in a beaker on the water-bath until all is dissolved, allow to cool, and pour into 400 c.c. cold water. Shake out the solution with petroleum spirit twice over, wash the extract thus obtained first with half its volume of 5 per cent. caustic alkali solution, then four times with one-third volume cold concentrated sulphuric acid, and at last with water, to remove the acid. Distil the petroleum spirit off in a tared flask, and weigh the residue.

It should be stated that the anthraquinone test, even in its most perfected form, does not give absolutely reliable results. Sometimes a certain description of quinone, which is as beautifully crystallized as possible, and cannot be distinguished by any outward marks, yields very inferior alizarin. The cause of this is as yet unknown; but it is most likely that the quinone

in such cases contains not merely pure anthraquinone, but also the derivatives of hydrocarbons other than anthracene, which are so similar to anthraquinone in appearance and chemical properties, that at present no means are known of separating them from anthraquinone itself. Some authorities have asserted that these inferior quinones are more easily soluble in glacial acetic acid; but no proof of this has been given, and we must hold this question as not yet solved.

Mr B. Nickels has communicated to Mr Allen the following process for testing anthracene, employed at some alizarin-works, of which the aim is to work as closely as possible according to the method of oxidation pursued on a manufacturing scale.

With this view, the oxidation is carried out in very dilute liquids, under which conditions the anthracene is converted into anthraquinone, while the foreign hydrocarbons suffer but little change. On subsequently treating the product with sulphuric acid, the unoxidised hydrocarbons are converted into soluble substances, and a nearly pure anthraquinone results, which may be obtained perfectly pure by a second treatment with acid. In experienced hands and with careful manipulation, this miniature factory-operation gives constant and very accurate results.

The chief source of error is incomplete conversion of the anthracene itself, and its consequent solution and loss on treating the crude anthraquinone with sulphuric acid; but this can be guarded against by a microscopic examination of the oxidation-product. The following are the details of the process:— Ten grammes of the sample of anthracene are ground to an impalpable powder in a mortar; 20 g. of potassium bichromate are added, and the whole is thoroughly mixed by grinding. The mixture is transferred to a large porcelain dish, 1 litre of water added, and the liquid made to boil. Thirty grams of sulphuric acid are diluted with about an equal measure of water, and added in successive small portions during about one hour, the liquid being kept constantly boiling and frequently stirred. The boiling is continued for three hours after the whole of the acid has been added, care being taken to replace the loss by evaporation by adding boiling water, as it is only in such dilute solution that the anthracene can be converted into anthraquinone,

with simultaneously oxidizing the accompanying substances. The liquid is next filtered, and the filter washed with hot water till all traces of chromium-salts have been removed. The contents of the filter are then dried at 100° and weighed. The weight obtained represents the yield of "crude factory anthraquinone," and may contain from 40 to 50 per cent. of the pure substance. Before purifying this crude product, a minute quantity of it should be dissolved in hot benzene and a drop of the solution placed on a glass slide. After allowing the dissolved matters to crystallize, a glass cover is applied, and the slide observed under the microscope. Unoxidized anthracene, if present, assumes the form of sharp, tabular, overlaying plates; while the anthraquinone will be in the form of distinct needles and stellated groups. Naphthalene is the only associated hydrocarbon which at all simulates anthracene, but with a little care it is readily distinguished. The other bodies likely to be present assume more or less characteristic forms, which cannot be confounded with anthracene. Examined with the polariscope, the appearances of anthracene and anthraquinone are extremely characteristic. If no unoxidized anthracene be detected under the microscope, the purification of the crude anthraquinone is proceeded with as follows:—

The crude anthraquinone is next treated in a small shallow dish with four times its weight of strong sulphuric acid; and the mixture is heated in the water-oven for about an hour and a half, being frequently stirred during that time. The capsule is then placed in a box, or under a bell-jar, side by side with a larger dish of boiling water, so as to maintain a moist atmosphere, which causes the gradual dilution of the acid and facilitates the crystallization of the anthraquinone. After twelve hours the capsule is removed and immersed in about 500 c.c. of water, which is then boiled. After cooling, the liquid is filtered, the residue washed till free from acid, and then treated on the filter with a dilute boiling solution of caustic soda (sp. gr. 1·04), till the filtrate runs through colourless. The alkali is then washed out with warm water, and the substance on the filter dried at 100° C. and weighed. The product has a greenish-grey or slate-grey colour, is highly crystalline, and contains from 80 to 95 per cent. of real anthraquinone. A known weight of it (about 1 g.) is further purified by heating it in the water-oven

for ten minutes with ten times its weight of strong sulphuric acid. The product is exposed to a moist atmosphere, dissolved in water, filtered, treated with alkali, etc., and weighed in a manner exactly similar to that previously adopted. The usual precautions respecting the treatment of the anthraquinone on the filter should be observed here. The weight of pure anthraquinone obtained is calculated first on the grey product, and then on the original sample, or intermediately on the crude anthraquinone, if some of the latter was not recovered from the benzene solution used for its microscopic examination. The pure anthraquinone found, multiplied by ·856, gives the real anthracene in the sample.

Lastly, we shall mention a plan for *estimating the quantity of anthracene present in tar*, although it does not appear to be very correct, the quantity of tar worked upon being so very small. C. Nicol[1] distils 20 g. of tar, and collects the vapours in a U-tube kept at 200° C. by means of a paraffin-bath. Here the more volatile oils go away, whilst anthracene, etc., remain behind. Since a little remains in the neck of the retort, this is cut off, the glass is pounded and added to the distillate in the receiver. This is now dissolved in glacial acetic acid, and the anthracene estimated by Luck's test. (In testing tar, I distil at least 1 litre at a time, and estimate the anthracene in the oil coming over between 270° and the end of the distillation.)

Analytical methods for Carbazol and Phenanthrene.[2]

Carbazol can be estimated in two ways. Either remove the basic compounds by means of warm, dilute sulphuric acid, estimate in the residue the nitrogen by Kjeldahl's method and from this calculate the carbazol. Or else proceed in the following manner:—

In a very thick-walled steel crucible, Fig. 144, holding 80 c.c., in whose very thick sides there is a hole drilled for a thermometer, 40 g. caustic potash of 80 to 85 per cent. KOH are melted. Keep the temperature at 180° to 200° C., and with constant stirring introduce 20 g. of crude carbazol (or crude anthracene). Take away the top part, put any matter sublimed into it back into the crucible and volatilize the anthracene and

[1] *Z. anal. Chem.*, 1876, p. 318. [2] From *Muspratt-Bunte*, viii., 71.

other concomitant substances at a temperature *not exceeding* 270° C. For this two hours suffice in the case of high per cent. carbazol. Longer heating should be avoided. Triturate the cold melt with hot water and add dilute sulphuric acid until the acid reaction is distinct. Put the carbazol thus set free on to a filter, wash and dry. The product is usually of a dark colour and must be purified with toluene, of which for high per cent. carbazol 600 to 800 c.c. are required. Pour the boiling toluene solution through a pleated filter and wash the flask and the filter with a small (measured) quantity of boiling toluene. From the (usually brown) solution part of the carbazol crystallizes out; this, after twelve hours' standing at 14 to 18° C., is drained by aspiration on a filter disk and weighed. The filtrate is measured at 17° C., and for each 100 c.c. 0·48 g. carbazol is allowed as contained in the solution. In the end 0·5 g. carbazol must be added as a correction of the quantity found.

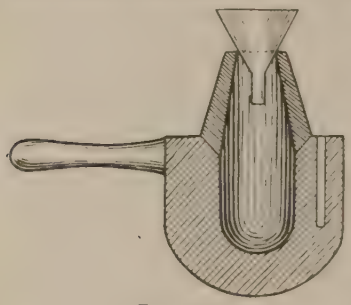


FIG. 144.

Estimation of Phenanthrene.—This is more difficult than that of anthracene and carbazol. The following method (communicated by Kraemer and Spilker) gives tolerably reliable results only in the case of a material rich in phenanthrene. For estimating it in crude anthracene the percentage of phenanthrene is increased as follows:—Dissolve 1 kg. crude anthracene in 2 kg. toluene and allow to crystallize at the ordinary temperature, with frequent stirring for six hours. Separate the liquor after drawing it off by a vacuum pump and washing with 200 c.c. toluene from the anthracene and carbazol, which had been separated as crystals, and remove the toluene by evaporation. The residue thus obtained is submitted to fractional distillation, and the product passing between 280° and 340° C. is considered as rough phenanthrene and treated as follows:—20 g. of it is heated with a solution of 30 g. picric acid in 300 c.c. dry xylene in a flask with reflux cooler. The crystals separated after standing for twenty-four hours, during

which time the mass should be strongly shaken up several times, are collected on the vacuum pump, dried, and weighed as crude picrate. The mother liquor is diluted with 50 c.c. xylene, and in it once more 20 g. crude phenanthrene and 30 g. picric acid are dissolved. The difference between the quantity of rough picrate now obtained against the weight of the first crop of crystals shows the rough picrate dissolved in 250 c.c. xylene. From the solubility factor thus obtained and the weights of the crops of crystals we find the total weight of the rough picrate formed from 40 g. of the crude phenanthrene. A weighed portion of this is recrystallized from 95 per cent. alcohol. To the weight of the pure picrate, separating in the shape of shining yellow-red needles, that dissolved in the alcohol (20 g. for 750 c.c. 95 per cent. alcohol) must be added. It is better to convince one's self of the purity of the last-obtained picrate, by decomposing it with ammonia, washing the hydrocarbon with dilute sulphuric acid (to remove any acridine possibly present), and weighing the remainder; 100 picrate = 43·7 phenanthrene. In the case of very impure phenanthrene it is preferable to work upon 30 g. each time, allowing 45 g. picric acid and 200 c.c. xylene (in lieu of 50 c.c.) after the first cystallization. The difference of both crystallizations now represents the solubility of rough picrate in 100 c.c. xylene.

The following *qualitative reactions* for the *Discovery of carbazol and phenanthrene* are given by Behrens.[1] For carbazol extract with acetic ether in the cold, allow the liquid to evaporate, and put the residue on to a watch glass, with a few drops of acetic ether; the carbazol, remaining behind on evaporation on the margin, when being moistened with a drop of nitrobenzene and phenanthrene quinone, yields characteristic copper-coloured scales. For phenanthrene, extract with benzol and test with a solution of a dinitrophenanthrene quinone in nitrobenzene (*cf.* also, *Chem. Centr.*, 1901, i., 796).

[1] *Chem. Centr.*, 1902, ii., 540.

CHAPTER VIII

CREOSOTE OIL

In this chapter we treat of the employment or further refining of those distillates from coal-tar which are midway between carbolic oil and anthracene oil. These are, in the first place, the fraction of coal-tar distilling directly between 240° and 270°, and besides, from either side, the residues from the manufacture of carbolic acid, naphthalene, and anthracene. Practically everything which cannot be used for any other purpose is run into the creosote-oil well.

Since there are often very large stocks of this oil accumulating at the works, there must be correspondingly large store-tanks or wells, which need not be covered over, as the oil is not very volatile and the rain-water floats on the top of it, whilst the pumps take it away from the bottom. Still it is safer, as a precaution against fire, to cover up the tanks. At La Villette, the creosote oil is kept in large upright cylindrical tanks, standing on brick pillars over a water-tank visible and accessible from all sides. Thus any leakages are noticed at once, and in any case the oil is prevented from penetrating into the ground. Where this is of no great consequence, the oil-tanks are, as a rule, partially or entirely sunk in the ground. They are better if made of boiler-plate than of brickwork set in cement.

It is advisable to fix a steam-pipe in the well, so that the naphthalene crystallizing out can be dissolved again before any large quantity is sent out.

Directly after the distillation, the creosote oil is pumped or forced into these tanks, where it is allowed to cool, and where most of the naphthalene separates. Creosote oil rarely contains less than 40 per cent. naphthalene, sometimes more. It therefore solidifies to a great extent on cooling, and usually exhibits

a dense, continuous covering of naphthalene. Oil obtained from tar, produced from material containing much cannel coal contains less naphthalene and more of the higher phenols. The bottom of the coolers is provided with a tap, which before the entrance of the oil is closed by means of a wooden plug. After cooling, this plug is removed and the liquid portion of the oil is now conveyed into the principal reservoir. The naphthalene is shovelled out into drainers; its further treatment will be described later on. Some people consider this naphthalene from creosote oil as unsuitable for purification, and only fit for softening the pitch or burning into soot. But this is a prejudice; by proper treatment it can be purified as well as the naphthalene from carbolic oil.

Properties.—Creosote oil, also called heavy oil or dead oil, is, in the fresh state, of a light greenish-yellow colour and strongly fluorescent, and is rendered still more fluorescent by the action of air and light. After some time it turns much darker and appears bottle-green by reflected, dark red by transmitted light. As the distillation proceeds, it becomes gradually darker and more consistent. Its smell is extremely characteristic—unpleasant, almost nauseous; it is probably caused by sulphur compounds not yet isolated. It is as thick as ordinary oil, and at first has also an oily touch, but soon acts upon the skin by its acids. It is always heavier than water; the specific gravity of its last portions is 1·070. The average sp. gr. is about 1·04.

The following bodies have been found in creosote oil:—naphthalene, α- and β-methylnaphthalene, tetrahydronaphthalene, diphenyl, acenaphthene, anthracene, phenanthrene, and the hydrocarbons coming in between these; phenol, cresol, more especially xylenol and α- and β-naphthol; aniline, quinoline, isoquinoline, and all the other bases mentioned in Chapter III. (pp. 228 *et seq.*). Only few of these substances are liquid, and it is certain that many more substances of a low fusing-point, as yet undiscovered, must exist in the liquid part of creosote oil.

We get an important insight into the nature of creosote oil (as well as anthracene oil) by the following results, obtained by Watson Smith from the distillation of Lancashire tar. Sample No. 1 was taken after 150 gallons had come over; No. 2 was a sample of the next 100 gallons; No. 3, of the next 100 gallons; No. 4, of the first "red oils"; No. 5, of the last oils.

No. 1 was of light colour, and on cooling was almost entirely solidified by the crystallization of naphthalene.

No. 2. Yellowish oil, with few crystals of naphthalene.

No. 3. Quite similar.

No. 4. Red oil, with but little deposit.

No. 5. Red oil, solidifying on cooling.

All contained a little water. Each of the samples was distilled, with the result given below, in percentages by volume (N signifies that, on cooling, naphthalene began to crystallize; O, that all remained liquid; A, that anthracene began to crystallize).

Temperature.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
	Per cent	Per cent.	Per cent.	Per cent.	Per cent.
Up to 180°	1·0	...	6·6	1·0	2·7 O
„ 210°	6·3 N	...	4·7 N	2·0	1·1
„ 220°	10·0	16·0 N	1·6	8·3 N	0·7
„ 230°	12·0	5·5	7·6	2·0	0·7
„ 240°	14·3	13·8	1·8	4·7	0·9
„ 250°	13·3	9·8	8·3	... O	3·3
„ 255°	...	...	...	...	..
„ 260°	9·3	4·9 O	9·3	9·7	0·7
„ 270°	7·0 O	8·9	1·6 O	12·0 A	1·8
„ 280°	4·3 A	4·9 A	8·7	8·7	1·8 A
„ 290°	3·7	3·5	6·6 A	5·4	1·8
„ 300°	3·7	3·8	11·3	4·3	5·9
„ 310°	3·7	2·1	4·5	3·0	12·0
„ 320°	3·7	2·8	1·3	7·3	8·2
„ 330°	...	...	...		4·0
„ 335°	...	...	...		
„ 340°	...	2·8	...	6·0	
„ 345°	...	...	...		
„ 350°	...	2·1			
„ 360°	...	...	1·6	18·0	
Above 360° :—					
Yellow crude anthracene	7·1	4·8	18·0	...	34·0
Orange or red substance	...	1·8	4·3	5·3	16·0
	99·4	87·5	97·8	97·7	95·6
State of the pitch remaining behind on rectification	good	very good	half coked	hard	beginning to coke
TOTALS.					
Crystallizing naphthalene oils	66·2	45·1	33·3	15·0	0
Not crystallizable oils	7·0	13·8	10·3	9·7	11·9
Anthracene oils	26·2	28·6	47·6	70·0	83·7

Redistillation of Creosote Oil.

This operation was for a long time avoided at most tar-works, as causing more trouble and expense than it was worth, and it was principally performed at some of the Scottish works. Recently it has come into more general use on the Continent. Its object is, of course, to separate as much of the more valuable constituents as possible.

The redistillation of creosote oil is usually performed in stills just like ordinary tar-stills; possibly in some cases with the employment of a vacuum. When distilling under ordinary atmospheric pressure, we obtain at first a very little "light oil" like that described on p. 364, then a little more "carbolic oil," but principally what may be called the first and the second "naphthalene oil," the limit between these being taken when the thermometer indicates 210° to 215° C. The "first naphthalene oil" on cooling solidifies to a great extent into naphthalene, almost of pure quality, about which we shall say more in the next chapter. The "second naphthalene oil," boiling up to 280°, also separates much naphthalene on cooling, but in a less pure state, containing methylnaphthalene and acenaphthene. The residue left in the still contains a little anthracene, and is worked up with the anthracene oil, as described in Chapter VII.

When the "first naphthalene oil" has cooled down, the solidified naphthalene is separated from the *liquid oily portion* (which may amount to one-half or a little more of the whole). This filtered oil contains, besides hydrocarbons, a few per cent. of tar bases which may be extracted by an acid, and a large quantity, say 25 per cent. of *phenols*. These make it valuable for disinfecting purposes, but in its crude state it would be frequently inconvenient to apply. We shall see below how this is remedied by the production of emulsions, etc.

Sometimes the "first naphthalene oil" is again redistilled, in order to obtain products containing a higher percentage (up to 50 per cent.) of phenols, employed for disinfecting purposes, or as an addition to the solution of zinc chloride for pickling timber.

The "second naphthalene oil" is also, after cooling, separated into a solid portion (impure naphthalene, *vide supra*) and a

liquid portion which is employed for pickling timber as described below.

Wurtz[1] recommends the following treatment:—The heavy oil is distilled in boilers holding 1000 to 2000 litres; and the following are collected: 1st, the products below 120°, which go to crude benzol; 2nd, the products between 121° and 190°; 3rd, the residue, which goes back to the tar. The second fraction [between 121° and 190°?] is washed with acid and alkali, and is then sold for lubricating, or for pickling timber, or else it is converted into an illuminating-oil. For this purpose the naphthalene should be removed by treating with 10 per cent. concentrated sulphuric acid, then with water, then with 6 per cent. concentrated solution of caustic soda. The oil is now rectified; and the distillate is agitated with ferrous sulphate (*vide infra*). The oil thus purified is sold as "huile sidérale."[2]

Rohart (Ger. P. 14924) heats heavy coal-tar oil, crude petroleum, etc., mixed with lime, in a still for several hours, and then submits the mass to distillation.

Frank (Ger. P. 139843) heats completely dehydrated coal-tar oil with 5 to 10 per cent. brimstone to 220° to 250°, until the evolution of H_2S ceases and a deep brown oil has been formed which is much more viscid, less volatile, and has a stronger preserving and disinfecting power than the original oil.

The pyridine bases are sometimes removed from creosote oil by a special treatment, but we must refer for this to the next chapter, especially as these bases form a valuable constituent in creosote oil for preserving timber (*vide infra*), and therefore ought not to be removed from it when using it for that purpose.

Removing the smell.—To remove the disagreeable smell of tar oils used for disinfecting purposes is the object of various inventors. This nauseous smell is principally caused by certain sulphur compounds. A very common proceeding is shaking up with a solution of ferrous sulphate, say 4 per cent.

[1] *Matières colorantes*, p. 33; *Dictionn. de Chimie*, i., p. 651.

[2] I have not been able to discover that any "huile sidérale," made in the way described by Wurtz or in any similar manner from coal-tar oils, is sold anywhere. It is possible that in this case again there has been some confusion with paraffin oils: but even if it be otherwise, we can only say that the above process must have been discontinued long since, as at the present prices of illuminating-oils it could not possibly be remunerative.

The Rütgerswerke (Ger. P. 155585) distil the oils with 1 per cent. lead acetate.

Deichler applied for a German patent (D14576) for treating heavy tar oils with formaldehyde, to remove the smell, but this was not granted, as being in collision with a patent of the Rütgerswerke (Ger. P. 147163) which prescribes the employment of aldehydes and ketones, especially formaldehyde (formalin), with addition of acid or alkali and heating by steam to about 90°. Part of the smelling compounds form with the aldehyde non-smelling condensation products remaining behind in the oil, and other volatile compounds of this kind are driven out by the steam.

A *disinfecting powder* is obtained from creosote oil or "first naphthalene oil" by mixing it with about four times its weight of dry hydrated *lime* (preferably quicklime which has been hydrated by lying in the air, and fallen into powder). This mixture after a short time takes a brick-red colour, by the formation of rosolic acid, etc., and is much employed in stables, railroad cars, etc., etc.

Emulsions of Creosote Oil or its Distillates.

Such are frequently prepared in order to convert these oils into mixtures, partly soluble in water (the solution with the remaining portion forming emulsions which are stable in this state for a long time without any separation of the constituents. This can be done in various ways. (One of these consists in mixing the oil with *soft soap* (potash soap), a process first recommended, it seems, by Pettenkofer, but probably practised some time before in some places. Such a mixture is sold by the name of *Creoline;* but the same name is also given to a mixture of crude creosote oil with sulphonated compounds of the same, both of them possessing the property of yielding with water a very slowly settling milky fluid. This "creoline" is principally used in veterinary practice against the scab or mange of dogs and sheep, sometimes even as a medicine for inner use of animals and men. Another name for the compound, obtained with soft soap, is *Sapocarbol. Lysol* (Dammann's Ger. P. 52129) is the same, with addition of saponified linseed oil or rosin (*cf.* Chapter VII.). This form is decidedly preferable to that obtained by the action of concentrated sulphuric acid (see below), since

this produces a greasy mixture of sulphonated phenols and hydrocarbons, quinoline sulphate, and insoluble oils, from which on dilution with water or ferrous sulphate solution very disagreeable tarry masses are separated (Kraemer and Spilker, p. 61). Spalteholz (Ger. P. 169493) employs for the purpose of preparing the tar-oil emulsions an alkaline solution of casein, preferably with an addition of a small quantity of rosin. It is claimed that these emulsions are not destroyed by the salts contained in ordinary water, as is the case with creoline, lysol, etc. The same inventor later on (Ger. P. 170332) recommends for the same purpose preferably the products obtained from casein by treatment with alkalis, acids, or by fermentation, always in an alkaline solution.

The Berliner Holz-Comptoir (Ger. P. 117263) employs a soap-solution of tar oils " of the well-known kind " for thoroughly impregnating timber, as it penetrates into this right into the centre.

The same firm (Ger. P. 139441) produces a lasting emulsion from tar oil and zinc-chloride solution, by mixing 5 to 50 per cent. wood-tar to the creosote oil, adding the aqueous solution of $ZnCl_2$ and passing air through the mixture for some time at boiling heat.

The same firm (Ger. P. 152179) has found that the desired result is obtained in much shorter time, by first blowing air through the mixture of creosote oil and wood-tar for a short time, and then gradually adding the $ZnCl_2$ solution, always stirring by air. In this case the temperature need be kept only at 60° to 70° C.; the mixture is more durable, and can at once be drawn or forced into the impregnating vessels.

A very much employed process for producing emulsions from heavy tar oils, consisting of a mixture of actually dissolved compounds with oils in a very fine state of division, is the treatment with *sulphuric acid*, by which the alkaline compounds (pyridines, etc.) are converted into salts, the phenols and some of the hydrocarbons into sulphonated derivatives soluble in water, and holding the undissolved oils in a state of suspension which lasts for a long time without any separation from the aqueous portion.[1] These emulsions may be entirely fluid

[1] According to a private communication from G. Kraemer, the sodium and potassium sulphonate of acenaphthene and phenanthrene are most efficient in forming such emulsions.

or of a more gelatinous kind, and they are, like tar-oil emulsions, produced in other ways, employed for pickling timber, as cooling agents in the drilling of iron, for treating textile fabrics, for laying the dust in public roads,[1] and other purposes.

Knoll & Co. (Ger P. 106500) treat tar with concentrated sulphuric acid at 100°; the reaction products are insoluble in water, but can be converted by alkali into solutions of almost neutral reaction.

Boleg (Ger. P. 122451) produces tar-oil emulsions by mixing the tar oils with rosin oil, and washing with steam and caustic-soda solution, separating from the rosin-soap solution, oxidizing with air or ozone, and in the end treating with steam at a plus-pressure of 1 to 1½ atmospheres. A further patent (Ger. P. 129480) prescribes regulating the viscosity of the oils, after being made soluble in water by the addition of 50 to 60 per cent. condensed water, with a little gelatine, and then treating in the oxidation apparatus at a slowly rising temperature (115° to 125° C., according to their specific gravity) with compressed air until the mixture has become perfectly clear. This process is declared by Künkler (*Seifensieder-Zeit.*, 1902, p. 510) to be quite useless.

"Westrumite" is a preparation, like Boleg's, used for watering public roads.

A further patent of the Boleg Company (Ger. P. 155288; B. P. 22091, 1903) prescribes treating the oils as in Ger. P. 122451, mixing with aromatic hydrocarbons, previously treated with air or ozone at a temperature of 50° to 70° C., with application of compressed air, heating the mixture to a pressure of 1 to 1½ atmospheres in high-pressure boilers and slowly cooling down.

The very great advantages of tar emulsions over the oils themselves for preserving timber, etc., are forcibly pointed out by Seidenschnur in *Z. angew. Chem.*, 1901, p. 437.

Nördlinger (Ger. P. 168611) makes heavy tar oils more suitable for impregnating and disinfecting purposes by mixing them with neutral or acid metallic salts of fatty acids, beginning from propionic acid, up to caprinic acid, or the analogous salts

[1] According to *Asphalt u. Teerind. Zeit.*, iii., 271, this has been done successfully at Turin, but for this purpose the oil must be free from naphthalene.

of the acrylic acid series, or solutions of these salts. These salts are more easily soluble in tar oils than the acetates, and their antiseptic action is consequently greater, while they are less easily washed out.

The Aktien-Gesellschaft für Teer- und Erdöl-Industrie (Fr. P. 309807, 1901) find that the salts of phenanthrene, mono- and disulphonic acids act as solvents for cresol, and so do the sulphonates of other tar hydrocarbons and of carbazol. The solutions are valuable as disinfectants or for pickling timber.

Further patents for tar-oil emulsions have been granted as follows:—Spalteholz (Ger. Ps. 170332 and 169493); van der Ploeg (B. P. 7699, 1905); F. Saint-Hilaire and E. Grousseau (Fr. P. 353663, 1905).

Pitch.

Pitch is made from creosote oil by various processes.

Nördlinger (Ger. P. 171380) employs the same process for tar oils as has been described in Chapter IV., viz., a treatment by air at 120° to 150° C.; *cf.* p. 292. The same is to be said of the processes of Wendriner (Ger. P. 170932, p. 292) and the Société anonyme des combustibles industriels (Ger. P. 161950; B. P. 16182, 1905, p. 292).

Mixtures of Creosote Oil with other Substances.

Bowden & Dodd (Ger. P. 126623) employ heavy tar oils, distilling between 260° and 280° C., to mix (in the proportion of 11 per cent.) with rosin, fatty oils, and soapstone for the production of a water-tight and insulating compound.

Bilfinger (Amer. P. 729838) treats creosote oil with dry powdered alkali, air, and lead oxide, and then mixes it with cotton-seed oil, to produce a substitute for linseed oil.

Uses of Creosote Oil (heavy tar oil).

Some of these have been already mentioned in previous chapters, because they coincide with the uses of raw tar or anthracene oils. We mention of these:—The softening of *hard pitch*, p. 432; the preparation of *varnishes*, p. 441; the burning for *lampblack*, pp. 295 and 463.

The application as *fuel*, p. 251. We add that the use of *tar oils* for this purpose is specially treated by Rispler (*Chem. Zeit.*, 1904, 157), who describes a spray-apparatus used for this

purpose; by Pietrusky (*Z. angew. Chem.*, 1905, 343) especially for the chlorinating roasting of sulphur ores, which by this means can be done in 40 minutes, whereas by firing with wood from 2½ to 3½ hours are required. In 1904 the first tar-oil tank-steamer was put into duty by the Imperial German marine-office, in order to make the men-of-war independent of the tank stores on land.

A burner for tar oils was patented by M'Murtrie (Ger. P. 163164).

For *explosion motors* creosote oil is proposed by Boswell (B. P. 22853, 1904), and by Albone & Boswell (B. P. 24449, 1904). *Cf.* also Kutzbach, in *Z. Verein. deutsch. Ingen.*, 1907, p. 521, and Riepel; *codem loco*, p. 613.

Employment of Heavy Oils as Lubricants.

This can be efficiently done only after removing the phenols (acids), which promote friction. Naphthalene also will hardly be adapted to promote lubrication. But the mixture of non-solidifying oils, which come before and along with anthracene, is really a lubricant, at least after proper treatment, and this sort of grease is pretty extensively used at collieries, etc., although the heavy paraffin and petroleum oils and rosin oil are far superior lubricants, and are nowadays cheap enough to make the employment of coal-tar oils superfluous.

In order to prepare the latter for this purpose, the phenols (commonly called "acids") must be removed. This would be done effectually by treatment with caustic soda; but as this is mostly too expensive, the cartgrease-manufacturers treat the oils with lime, similarly to rosin oils, with which they are generally mixed. Thenius[1] prescribes gradually adding to a hundredweight of crude rosin oil, contained in a retort, 56 lb. of slaked lime, and heating, with agitation, till the whole is dissolved, then distil for an hour, condensing the vapours. The mass is now allowed to settle and the clear portion is run off. On the other hand, 1½ cwt. of dry slaked lime is mixed in an open pan with ½ cwt. of rosin oil and ½ cwt. of heavy coal-tar oil freed from acids; the mass is stirred and heated till it is quite homogeneous, and is then allowed to cool while being

[1] *Verwerthung des Steinkohlentheers*, p. 82. (This prescription is considered of very doubtful value by competent authorities.)

constantly agitated. From each of the two mixtures thus prepared ½ cwt. is taken and mixed up in a pan; and, with constant stirring, a third mixture is added, consisting of 23 lb. of melted ozokerite, ½ cwt. of heavy coal-tar oil free from acids, and ½ cwt. of heavy rosin oil. The latter mixture is added when it has cooled down to some extent, but before it has solidified. It may be coloured yellow with a few pounds of turmeric, or blackish blue by lampblack.

Thenius also describes another kind of cartgrease, made of a mixture of a tallow-soap, fish-oil, potash-soap, and coal-tar oil.

Dumoulin and Coutelle prepare lubricating oil by stirring up 2 cwt. of creosote oil, 11 galls. of water, 2 lb. of bleaching-powder, 2 lb. of soda-ash, and 1 lb. of manganese, settling twenty-four hours, decanting the clear liquid, distilling it, and mixing the distillate with one-fourth of its weight of rosin oil: this treatment is to remove the "gummy" part of the tar oils and to make them inodorous. Or else the oil may be distilled before adding the ingredients.

Employment of Creosote Oil for Lighting.

This oil has long been used during the construction of harbours, railways, etc., where the smoke caused no inconvenience. But this burning in open pans is a most wasteful, crude sort of illumination. The just-mentioned process of Dumoulin and Coutelle was intended to make creosote oil fit for lighting even dwelling-rooms; but that degree of success is very doubtful. In order to get a proper lighting-effect, it is indispensable to introduce a jet of air, which prevents the formation of black smoke and burns the soot. Hence everything depends upon the construction of the *lamps*. One of the best lamps for this purpose is the steam-jet lamp of Hartmann and Lucke;[1] shown in Figs. 145 and 146. The steam-jet serves not merely to convey the oxygen necessary for combustion, but also to decompose the carbon compounds, thus preventing the formation of soot and producing an intense light. This lamp can of course be employed for any cheap petroleum or tar oils, but is specially intended for ordinary creosote oil; it

[1] German patent No. 9195, 9th August 1879.

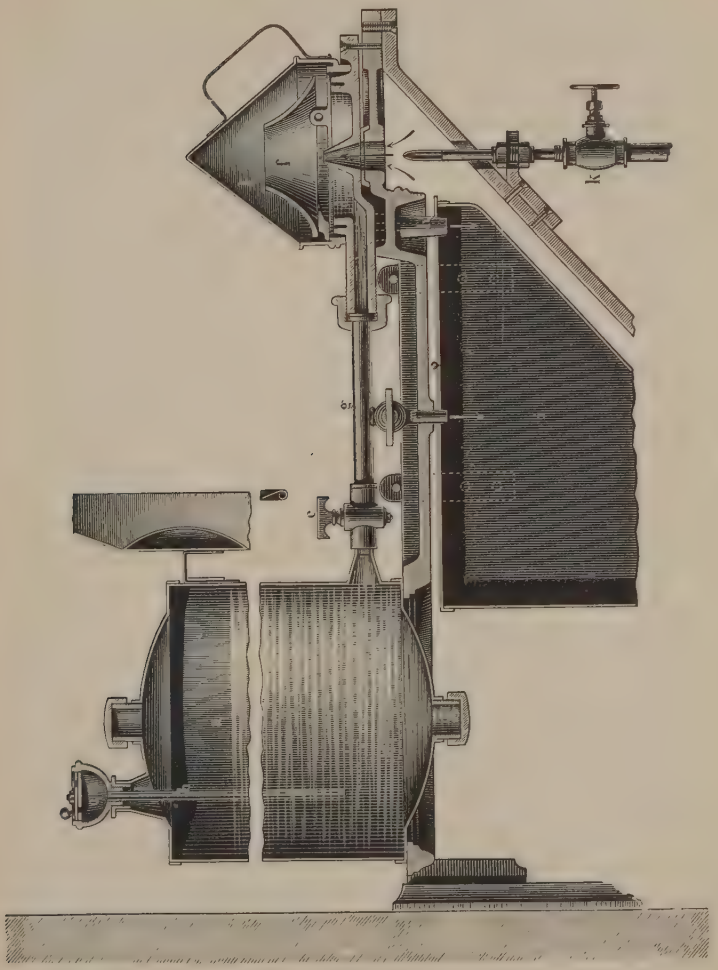


FIG. 145.

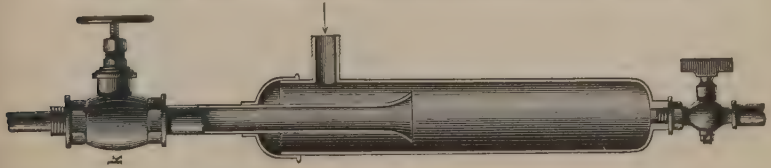


FIG. 146.

does not require a mechanical blast, but may be placed wherever steam can be had, and is thus principally adapted for lighting large factory workshops, yards, etc., but not for places which require a less intense and more divided source of light.

In the vessel *a*, filled with oil, is suspended the air-supply pipe *b*, ending at the top in a funnel, *c*, provided with a slide to regulate the supply of air to the vessel *a*. Hence the oil must flow out of *a* quite evenly, on Mariotte's principle, the pressure being constant. It flows through the cock *e* and the pipe *g* into the dish *d* (which must be mounted in a perfectly horizontal position), where it is lighted and then covered with the funnel *f*: as the oil is difficult to light, it is first covered with a little petroleum. Steam, first dried in the apparatus *k* (Fig. 146), is now, very slowly, admitted through the conical opening in the dish *d*. As soon as the oil burns equally all over the dish, which is brought about by regulating the steam-supply, the lamp requires no more attention. If by a wrong position of the slide at *c* the dish is supplied with more oil than can be burnt, the superfluous portion overflows into the annular channel round the dish and through the tube *h* into the vessel *i*. At first it is best to let it overflow; afterwards, when the oil has become hot, its supply is regulated so that the inner part of the dish always remains full. To put out the lamp, the cock *e* is shut (so that no more oil flows into the dish), the steam is shut off by the cock *k*, and the flame is extinguished by putting on the funnel-shaped cover *l*. The oil remaining in *d* and *g* is run into *i* by opening the tap *m*. This is a threeway-cock, which either conveys the oil to the burner or else discharges it into the vessel *i*.

The steam admitted underneath the dish *d* acts mechanically by forcing the air necessary for combustion into the flame, and also by aspirating the air from without through the openings beneath the funnel *f*. The steam also acts chemically upon the hydrocarbons, forming a gaseous mixture, which, on combustion, produces an extremely brilliant light and no soot. This is not attained by ordinary lamps, because in them, when enough air is admitted, the flame becomes hotter but not more luminous. The steam should be as dry as possible, and the condensed water must be allowed to run away.

Thus the tar oil burns without wick or chimney, preferably

in very large glass lamps with reflectors. Such a lamp gives a light of 20 ordinary gas-lights or 180 standard candles, with an hourly consumption of about $2\frac{1}{4}$ lb. of tar oil. The oil-vessel holds about 7 galls., so as to suffice for the longest winter nights. The lamps need no cleaning or repairing.

A more recent form of this lamp is shown in Fig. 147, $\frac{1}{12}$ natural size; this shape costs £5 including package, the glass

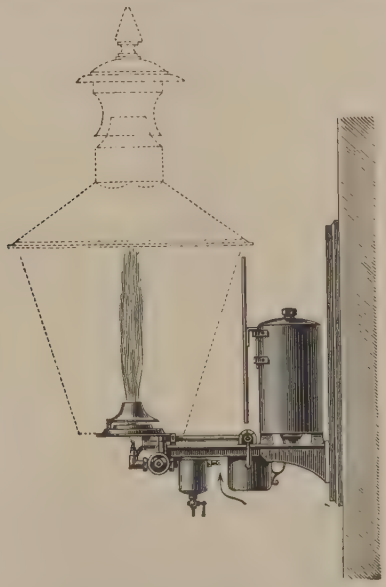


Fig. 147.

lamp £4. Where the carriage does not make the oil too dear, this light is much cheaper than gas-light.

Another apparatus for the same purpose has been patented by Messrs Lyle & Hannay (67 Great Clyde Street, Glasgow), under the name of the "Lucigen" (*cf.* p. 138). I owe the description of it to the kindness of Mr S. B. Boulton. It consists of an oil-tank or reservoir (Fig. 148), fitted with a special burner at the top of a tube, H, which can be made to any length. Into this reservoir compressed air is introduced by an india-rubber pipe, this material being used to make the "Lucigen" portable. On the compressed air being let into the tank at A (B

is a moisture-trap, C a blow-off cock), it forces the oil up through an internal tube, and, escaping at the same time through D, O

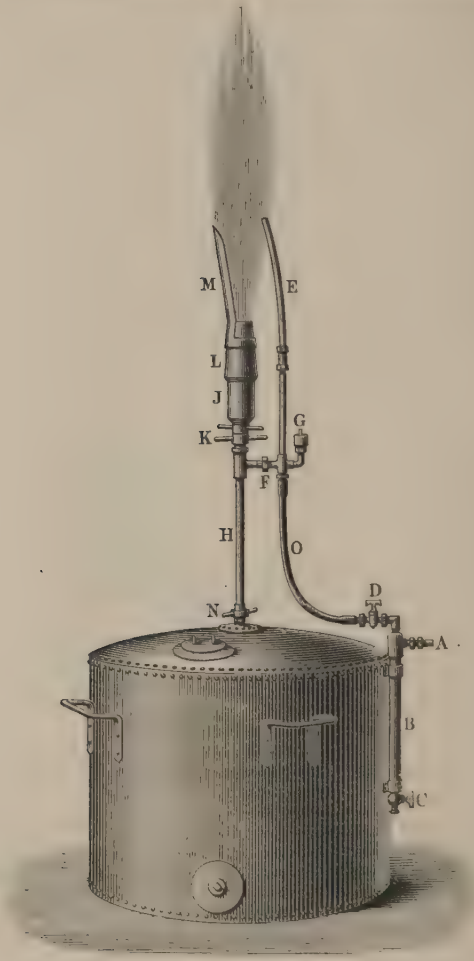


FIG. 148.

and E, with the oil in the burner J and combustion chamber L, produces a spray which is set on fire. M is a wind-guard, K and N regulating jam-nuts, G a safety-valve. The pressure at

which the air is forced into the accumulator is about 15 lb.; and this is sufficient to supply the whole of the lights. A light of about 2000 candle-power is given by the "Lucigen." The flame is large, and the light well-diffused, and the eyes are not dazzled by it. It is claimed by the patentees that the "Lucigen" is much more distributive in quality than the electric light, and that it does not cast such deep shadows; also that it is much cheaper, alike in cost and maintenance, than either gas or electric light. It can be produced by either air or steam at a nominal expenditure of power, and it does not require any neat adjustment of machinery. The oil used in the Lucigen is the refuse of chemical- and gas-works, and about 1 gall. per hour is consumed. Owing to the application of pressure, the "Lucigen," when burning, emits a sound resembling steam blowing off. This, in a confined building, would naturally be very disagreeable; but in the open air the hissing noise emitted is not very annoying. There is scarcely any smoke from the light; and the smell of the consumed oil is not offensive. The Lucigen burns equally well under heavy rain or spray. It does not need any lantern, and has no parts which can be damaged by rough usage.

An improvement upon the Lucigen light is Grube's "Oleo-vapour lamp," shown Fig. 149. The reservoir is filled by a pump, M, to three-fourths of its capacity, with creosote oil, the air above the oil being compressed, as shown by a pressure-gauge. Thus the oil is forced into the burner R, which, after being once heated up, automatically heats and vaporizes the oil. For this preliminary heating, which takes eight or ten minutes, some oily cotton-waste is burned on the plate C. Once the flame has formed, the vaporization is effected by it. The flame gives a fine, bright light, not so glaring as arc-light, without any soot; it consumes 6 litres of creosote oil per hour, and requires no attention except pumping the oil every two hours. Such lamps are made of from 1000 to 5000 candle-power.

A similar apparatus is Luther and Rose's "Portable Sun-light," described in the *Chem. Trade J.*, 1887, p. 202. A steel cylinder, tested for 9 atmospheres' pressure and provided with a safety-valve, holds the oil; it is surrounded by a cast-iron jacket. The oil is vaporized by means of a small coke-fire,

and is passed into the combustion-chamber, where air is introduced, without a blast or the like, in such quantity that the oil-vapour, issuing under a pressure of $3\frac{1}{3}$ atmospheres, is burned completely with a dazzling white light. The patentees manufacture lamps up to 3000 candle-power, and they state the cost = 1d. per hour for 1000 candles (?).

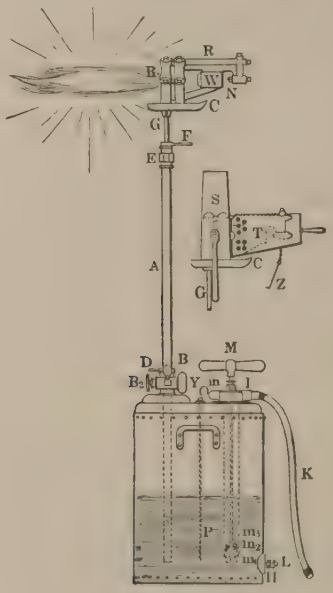


FIG. 149.

The employment of creosote oil for *carburetting gas* will be discussed later on, along with that of other tar oils (Chapter XI.).

Creosote Oil and preparations from it as Antiseptics.

Creosote oil contains from 10 to 20 per cent. and sometimes more than this of phenols, of which very little is carbolic acid, but mostly cresols and higher homologues. Even in the crude state it is an excellent antiseptic and is extensively used as such, in spite of its unpleasant smell and its slight solubility in aqueous liquids. Dusart has shown the strongly antiseptic properties of the portions distilling between 210° and 300°,

when freed from naphthalene. Before a separate fraction was taken in tar-distilling, which contains most of the phenols, together with naphthalene, pyridine bases, etc., of which we shall treat in the next chapter, it was usual to convert the creosote oil as a whole into a disinfectant, by various processes. Most of these are now applied to the crude carbolic oil, or even better to the crude mixture of cresols, from which carbolic oil on the one side, and naphthalene, etc., on the other side, have been removed. We shall therefore describe them in the next chapter under the heading : " Preparations from carbolic acid and cresols." *Cf.* also *supra*, p. 527 *et seq.*

Application of Creosote Oil for Pickling Timber.

This has become an industry of great importance, more especially for railway sleepers, telegraph poles, and piles used for harbour piers. By far the largest part of the oils distilled from coal-tar is employed for this purpose, and we can trace the first development of tar-distilling to the demand which arose for such oils consequent upon the introduction of Bethell's process (1838).

The history of timber-preserving in general, and that of the "creosoting" process in particular, has been given in several treatises, of which especially that by Mr S. B. Boulton ("On the Antiseptic Treatment of Timber," *Proc. Inst. Civ. Eng.*, 1883-84, vol. lxxviii., p. 4) contains much original matter ; the same subject is also treated in Adolf Mayer's *Chemische Technologie des Holzes* (Braunschweig, 1872), Buresch's *Der Schutz des Holzes* (2nd ed., Dresden, 1880), and Heinzerling's *Die Conservirung des Holzes* (Halle, 1882). To those treatises we refer for a description of the technical part of creosoting, which does not come within our domain, and for more detailed statements regarding this subject in general.

Tar and pitch were used for painting or smearing wood in the remotest antiquity ; special instances of preserving timber from decay are related in connection with the platform on which stood that wonder of the world, the statue of Zeus by Phidias, at Olympia, and with the famous wooden statue of Diana at Ephesus (Boulton, p. 5). The preservation of the Egyptian mummies may to a great extent be placed in the same category. But we must take a wide step in history

before we meet with any widespread application of antiseptics for wood. Apart from a few isolated trials with various antiseptics made during the eighteenth century, we find practically nothing done in this line till the beginning of the present century, although the records of the British Patent Office contain lists of almost every conceivable antiseptic from the year 1768 (Boulton, p. 8). But it is since the birth and growth of the railway system that the antiseptic treatment of timber has received its most important development. By the year 1838 the four systems of timber-preserving which alone are now employed were fairly before the public, and competing for the favour of engineers, namely:—(1) Corrosive sublimate, known since 1705, again introduced by J. H. Kyan; (2) sulphate of copper, known since 1767, principally introduced by Boucherie; (3) chloride of zinc, known since 1815, patented again by Sir William Burnett; and, lastly, (4) heavy oil of tar, afterwards called creosote oil, patented by John Bethell.

We shall, of course, occupy ourselves only with the last-mentioned process, which, moreover, has far outstripped the other three in importance, and in England has entirely extinguished its rivals. Vegetable tars, or extracts from the same, were used for timber-preserving, both in England and America, as early as 1756 (Boulton, p. 10). The first to mention the products of the distillation of gas-tar for impregnating timber was Franz Moll (B. P. No. 6983, January 1836). He proposed to employ, at the commencement of the operation, the oils lighter than water, which he called "Eupion," and afterwards the heavier oils, which he called "Kreosot." Both names were taken from Reichenbach's investigation of the products obtainable from wood-tar, as it was not known at that time what fundamental difference exists in the composition of wood-tar and coal-tar. Real creosote, in Reichenbach's sense, does not occur in coal-tar; but the phenol contained in the latter was for a long time confounded with Reichenbach's creosote. Moll's process, so far as the application of light oil was concerned, was manifestly unpractical; but the stimulus was now given for employing the products from coal-tar in that line, and in 1838 followed the practical introduction of the process by Mr John Bethell. The terms "creosote" and "creosoting," now generally used in this

connection, are thus due to Franz Moll; they do not occur in Bethell's patent, which contains a list of no less than eighteen various substances, mixtures or solutions, oleaginous, bituminous, and of metallic salts. Amongst them is a mixture consisting of coal-tar, thinned with from one-third to one-half of its quantity of dead oil distilled from coal-tar; and as late as 1849 Bethell's licenses mention the admixture of gas-tar. In those times inspectors frequently refused to allow the dead oils to be used without being thickened with tar (Boulton, p. 14), as it was not understood that the pitch was only an impediment to the injection. This must have been recognised very soon after. The dead oils came into use alone; and there crept into the specifications the contradictory prescriptions that the wood was to be creosoted according to Bethell's patent, but that the creosote was to be free from adulteration with coal-tar.

Coal-tar creosote has been recognised as superior to lignite oils, rosin oil, etc., because it contains not merely phenols, like these, but also basic substances which with the phenols and unsaturated hydrocarbons form resin-like combinations, filling up the cells and protecting them from destruction. Some German railway companies positively forbid the employment of creosote oil, containing upwards of 25 per cent. lignite oils, for pickling their sleepers.

The *apparatus* now universally employed for impregnating timber, both with creosote oil and chloride of zinc, was first introduced by Bréant, director of the Paris Mint, in 1831, who employed it for injecting linseed oil and rosin. The principle of Bréant's process was adopted by J. Bethell, and greatly improved by him and H. P. Burt. Their apparatus, as constructed above fifty years ago, has been adopted everywhere in all its essential features, and is minutely described in the above-mentioned treatises. It consists of a very strong, horizontal, wrought-iron boiler, 6 or 7 feet in diameter, 30 to 60 feet long, and $\frac{3}{8}$ inch thick. The timber is placed on iron bogie-frames, which are run upon rails into the cylinder, whose front is then firmly closed by a cover. The air is now exhausted till the air-gauge indicates about $\frac{1}{6}$ or $\frac{1}{8}$ of an atmosphere; communication is now opened by a cock with a tank holding the creosote oil, heated to a temperature of about 50°, at which it should be perfectly fluid. The oil at once rushes into the

vacuum and deeply penetrates into the pores of the wood, whilst otherwise the air contained in them would pertinaciously resist the entrance of the oil. When no more oil is sucked up, a force-pump is started, which presses more oil into the cylinder, till a pressure of 8 or 10 atmospheres has been attained. This is kept up for several hours; and the wood in this operation absorbs on an average nearly a gallon per cubic foot.

The plan of injecting creosote oils or similar substances in a state of vapour, which has been several times tried (Lukin, 1812; Franz Moll, 1836; Bethell, 1864, etc.), could not possibly answer. Timber is weakened by exposure to a temperature much exceeding 120°, and is seriously injured at 150°; but the boiling-point of creosote oils ranges from 200° to about 370°. Hence its vapours can only be injected into wood under such conditions of temperature and pressure as will destroy the value of the timber; and experience has proved this to be the case. Nor has the application of superheated steam, passed through creosote oils, met with much more success (Boulton, pp. 30, 31, and below).

One difficulty of the creosoting process is the *presence of moisture* in the timber to be preserved. In the fresh-cut state, or as it is taken from the timber-ponds, it is not in a fit condition for creosoting, and must be stacked first from four to six months. Many methods have been tried for artificially drying the timber, in order to do away with the necessity of long stacking, which is extremely cumbersome or even impossible when piles, etc., have to be sawn from larger logs, for immediate use in harbour-works, etc.; but they have all been abandoned, as, if the heat applied is really efficient in expelling the water, the woody fibre is sure to be injured in the process. Vohl[1] made a proposal which, if it were successful, would obviate the difficulty, by converting the creosote from an oily into an aqueous fluid; namely, adding enough solution of caustic soda to the creosote to make it miscible with water, impregnating the timber with this liquid, and ultimately "fixing" the creosote with a dilute solution of ferrous sulphate. But as this process was evidently never carried out on a manufacturing scale, nothing further can be stated respecting it.

Another way out of the difficulty is to apply the creosote oil in a heated state, so that the water contained in the timber

[1] *Dingl. polyt. J.*, vol. cxvii., p. 448.

evaporates during the operation. A process founded upon this principle, but evidently imperfect in other respects, was invented by Pelton, and, according to a report made by Ott in 1874,[1] seems to have been largely employed in America at that period. It consisted in placing the timber, in the green state, in iron cylinders, covering it up with creosote oil and heating this for some time up to 100° or 110°, until the water was evaporated, and running in fresh cold oil. This causes the hot oil, already contained in the cylinder, to penetrate into the pores of the wood, a partial vacuum being induced by the cooling. The apparatus is figured and described in detail in the work quoted. It is very doubtful whether in this way the impregnation will be thorough; the very imperfect vacuum, and the absence of pressure at the finish, make this very unlikely. Pelton's process does not seem to have been very successful, for, according to a communication from Mr S. B. Boulton, a committee of the American Society of Civil Engineers, in the report on the preservation of timber, presented and accepted at the Annual Meeting on the 25th June, 1885, does not mention Pelton's method among the many different processes described.

The object in quest, however, is completely attained by S. B. Boulton's process (B. P. No. 1854, of 1879). The timber is placed in the ordinary high-pressure creosoting cylinder (A, Fig. 150), which is provided with a somewhat high dome, *a*. After the air has been exhausted in the usual way, the creosote is introduced through the pipe *b* at a temperature a little above 100°; but it is not allowed to rise quite to the top, so that the dome *a* is always kept empty, and the creosote is not drawn through the exhaust-pipe. The boiler B serves to heat up the creosote. The exhausting process is continued, by means of the pump C, until all the moisture contained in the pores of the timber has been vaporized by the heat of the creosote oil, and has been drawn away in the state of vapour by the air-pump. As the temperature employed is much below the boiling-point of creosote, this liquid is not turned into vapour. The aqueous vapour is drawn through the dome *a*, is condensed by passing through the worm D, and the water is collected in the receiving-tanks E F, where the quantity extracted can be measured. The timber may be introduced quite wet; the water it contains

[1] *Wagner's Jahresber.*, 1874, p. 959.

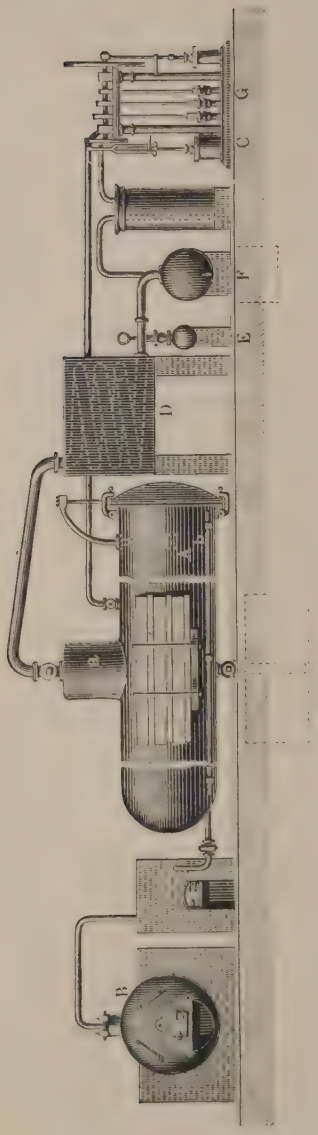


FIG. 150.

is replaced by creosote, as much as 50 galls. per load of timber, without ever subjecting the wood to a dry heat. The process of injection can then be completed by means of the pressure-pumps G in the usual manner.

Boulton's process involves a slight additional cost and a few more hours for dealing with very wet timber, but not so much time and money as is required for stoving the timber, apart from the risk of deterioration incurred thereby; while for drying by stacking the timber six months, the interest and the value of the place occupied must be set off against the cost of the new process.

A process patented by Blythe, of Bordeaux (Ger. P. 10423) essentially consists of injecting superheated steam into creosote oil, and allowing the mixed vapours of steam and creosote oil to act upon the wood contained in a closed boiler. The process has been extensively used in France, but with very unsatisfactory results.[1] A sleeper which, according to the process usually followed in Germany, would take up 18 kg. of creosote oil, absorbs only 11 kg. in Blythe's process.

[1] *Cf.* Claus, *Wagner-Fischer's Jahresber. d. chem. Techn.*, 1883, p. 1202, where many interesting details are given concerning the results of different methods of pickling timber.

The German process, as carried out in the various large establishments of Jul. Rütgers, is as follows:—The sleepers are exposed in stoves to a temperature gradually raised to 130° C., and are thus treated for at least four hours, until no more aqueous vapour is given off and the sleepers are uniformly heated. The sleepers are introduced while hot, being left on the same bogie, into the creosoting cylinder. After this has been closed air-tight, a vacuum at least as low as 55 mm. (= 2 in.) mercury is produced within thirty minutes, and is kept up another thirty minutes. The cylinder is now placed in communication with the tank holding the warmed-up creosote oil, and, after being filled with it, is brought under a pressure of at least $6\frac{3}{4}$ atmospheres for upwards of one hour. Beech-wood sleepers should be either stove-dried or steamed in as fresh a state as possible, before the sap has begun to ferment. Stoving is difficult, because beech-wood has a tendency to split; it is therefore preferable to steam the timber till the temperature exceeds 100° even in the interior, and to remove the sap during the same process by lixiviation. When the pickling is to be performed by aqueous solutions, the steamed sleepers are best submitted directly to the impregnating process; but in the case of tar oils, the timber must be first air-dried, which in spring or summer takes two or three months. Well-prepared and properly impregnated beech-wood sleepers do not suffer in comparison with those made of any other description of wood. The wood is impregnated all through; it remains hard and tough; and the bolts hold quite fast in it, as has been proved many times with rails which had been in use for a long time.

Chaligny and Guyot-Sionnest have constructed a *travelling apparatus for pickling timber*, mounted upon two railway trucks, which enables the pickling operation to be performed at every railway station (Armengaud's *Publication Industrielle*, 1884-85, vol. xxx., p. 295; *Dingl. polyt. J.*, vol. cclx., p. 75). Such apparatus, of their own construction, is also employed by Messrs Burt, Boulton, & Haywood in their French business.

Drittler (Ger. P. 75805) employs an apparatus for simultaneously exhausting the air and forcing in the pickling liquid. R. Schulz (Ger. P. 53854) and Liebau (Ger. Ps. 50295 and 52893) try to avoid the necessity of pickling at special works by

applying a small apparatus for that purpose to the felled trees themselves.

Altena (B. P. 15631, 1906; Ger. P. 175691) places the wood in trucks which are run on to a stage near the top of a vessel resembling a gas-holder. This vessel can be raised or lowered above a reservoir containing the impregnating liquid, by admitting or withdrawing compressed air from it. When it is in its lowest position, the charge of wood is completely covered by the liquid. Air is then quickly admitted so as to raise the vessel, and, at the same time, to force the liquid into the wood, the operation being repeated if necessary. Special means of regulation are supplied to guard against too rapid an ascent or descent of the vessel.

Many other apparatus have been patented for pickling timber, into which we cannot enter here.

The creosote treatment is also applied to sails, ship's ropes, fishing-nets, etc., and protects these better than the usual tarring. The objects are first "tanned" by treating them with a dilute solution of glue and then with a bath of tanner's bark. Thus glue is precipitated within the vegetable fibre, which is now enabled to fix the creosote oil in the subsequent treatment and retain it even in sea-water.

The advantages of pickling wood with tar oils, or "creosoting," are both chemical and mechanical. The principal chemical action of coal-tar creosote was formerly ascribed to its "acids" —*i.e.*, the phenols—which certainly coagulate albumen, and consequently render animal life impossible. This, together with the now universal supposition that putrefactive decay can only occur in the presence of microscopic organisms, whose vital process is an indispensable condition of it, would by itself explain why timber impregnated with phenol cannot decay, provided that the phenol is not removed again by washing, etc. Hence the value of creosoting oils would correspond to their percentage of phenols. But this opinion is generally contradicted now, and it is held that the "indifferent oils" participate essentially in the preservative action of coal-tar creosote. In any case the last-mentioned oils play a principal part in the *mechanical* effects of creosote oil, which are no doubt very important. The oil, being forcibly drawn into the wood by a vacuum and then driven in by high pressure, closes up all pores and, as it

were, agglutinates all the parts so that no water can penetrate, without which living organisms cannot develop and the wood cannot decay. Even larger insects and other vermin are kept away by the smell of creosoted wood. This smell, however, has its drawbacks. It is sometimes so strong in pits fitted with creosoted timber that the men suffer a good deal from it, and the demand has even been raised to forbid the use of creosoted timber for coal-pits, etc., for this reason. Nor must it be overlooked that the danger of fire in the pits is decidedly increased thereby. It is therefor advisable to paint the creosoted timber with a silicate-of-soda paint, or something like it which would both stop the smell and prevent any danger of fire.

There are many undoubted instances of creosoted timber when used for piers in salt water having successfully resisted even the formidable *Teredo navalis* during a long series of years; but there are also failures, sometimes in the same waters where the successful cases have occurred. The failure is caused either by the outer or creosoted part of the wood having been broken or cut off by the workmen in the process of construction, so that the worm could get into the inside of the timber; or by creosoting the wood in the wet state or imperfectly; or by employing creosote which is too thin, light, or volatile. Wood intended to resist marine insects should receive a heavier dose of creosote, and is better employed in the round state than squared, because the sap-wood more readily absorbs the creosote than the heart-wood, and thus forms a protecting girdle against the worm. (Private communication from Mr S. B. Boulton.)

Creosoted stakes in vineyards are said to keep out the *Phylloxera* (*Polyt. Notizblatt*, 1886, p. 304); but this does not seem to be quite certain. In the Hessian Rhine province, where all stakes are creosoted, that parasite has not been found, although it occurs in other places not far distant. The assertion that such stakes impart a creosote taste to the wine is absurd, and is entirely refuted by the experience gained in Hessia.

The Arad-Csanad Railway Co. (Ger. P. 53691) asserts that the pickling of timber is improved by following up the ordinarily used salts of iron, zinc, and copper by a rosin-creosote soap (creolin, p. 527). Similar proposals had been previously made by Vohl (p. 392), Kretzschmar (*Chem. Zeit.*, 1889, p. 31), and Wolniewicz (*ibid.*, 1889, p. 1089).

Clark[1] reports at length on the experience gained in America by pickling wood with coal-tar dead oil on the one hand, and with wood-tar creosote on the other. The former contains less water and is more easily treated in the creosoting cylinder. The wood-tar creosote is free from ammonia, less volatile, and less soluble in water, so that the advantages and drawbacks nearly counterbalance.

It has long been disputed what part is taken by the *naphthalene* in creosote oil. We know that it occurs abundantly therein, and crystallizes out on the cooling of the first fraction of this oil. Its quantity is increased by the residue from working the light oils for benzols, phenols, etc., which is extremely rich in naphthalene, going to the creosote oil. This, as it arrives at the creosoting-works, is often quite pasty with naphthalene. In the pickling process the oil is heated to 50 , so that the naphthalene is dissolved ; and only on the cooling of the pickled wood does it crystallize again, among the other constituents of the oil, the coagulated albumen, etc. It was formerly believed that this was injurious to the preservation of wood, perhaps on account of the naphthalene volatilizing and leaving empty spaces which might be filled with moisture and become breeding-places for putrefactive organisms. Hence several creosoting-works have fixed a maximum for the naphthalene, which causes great inconvenience to the tar-distiller, since very much more naphthalene is produced than can as yet be consumed.

But it seems that the objection to naphthalene in creosoting is quite unfounded. In the first place, naphthalene itself is undoubtedly a disinfectant and prevents the development of lower organisms. Secondly, as has been proved by Dr C. Meymott Tidy,[2] the total loss by evaporation of naphthalene is very small, and takes place almost exclusively during the first day or two after the wood has come out of the creosoting-apparatus. During the first and second day some naphthalene volatilizes from the surface of the timber ; but after this there is no more loss of weight, and the interior of the wood is quite unchanged. According to Dr Tidy, the naphthalene is useful both chemically and physically ; it cannot possibly do any harm ;

[1] *J. Soc. Chem. Ind.*, 1890, p. 1005.

[2] In an official (unpublished) report kindly placed at my disposal by Dr Tidy ; compare later on his report of 1883.

Specification made by . .	Dr Letheby.	Great Western Railway Co.	Chemin de fer de l'Est (France).	Chemin de fer de l'Ouest (France).	Chemin de fer de l'Etat Belge.	German Pickling Works "O."	German Pickling Works "M."
Spec. grav. .	1·045 to 1·055 at 60° F., but as nearly as possible at 1·050.	1·045 to 1·055 at 60° F.	1·030 at 35 C.			Between 1·020 and 1·055 at 15° C.	Between 1·055 and 1·100 at 15° C.
Deposit when cold.	Should not deposit any naphthalene at 40° F.	Should not deposit more than 30 per cent. at 40° F.	...	...	Not above 30 per cent. deposit (temperature not stated).	Entirely liquid at 15° C., as free as possible from naphthalene.	Free from naphthalene bottoms at 15° C.
Yield of coal-tar acids.	5 per cent. crude carbolic acid and other coal-tar acids.	10 per cent. acids, of which 5 per cent. crude carbolic acid.	8 per cent. phenol.	5 per cent. phenol.	...	20 to 25 per cent. tar acids soluble in caustic-soda solution spec. grav. 1·15.	At least 10 p.c. by volume of carbolic acid, estimated by treatment of the oils boiling up to 400° C. with caustic-soda solution spec. grav. 1·15.
Heat and quantity of distillate.	Should not yield less than 90 per cent. at 600° F.	Not less than 90 per cent. at 600° F.[1]	...	...	One third should distil at 200° to 250°, two thirds above 250° C.	To boil between 150° and 400° C. No more than 25 p.c. to distil below 235°, at most 1 p.c. below 125°. No fraction taken at intervals of 50° C. each, to separate more than 5 p.c. $C_{10}H_8$.	Nothing to distil below 150° C.; at most 25 per cent. up to 235°; to distil completely up to 400° C.
Heat and liquidity.	...	...	Should be perfectly liquid at 35° C.				
Further requirements.	...	...	...	Should be of "first quality."	...	Should be obtained entirely from coal-tar and possess a greenish-black colour.	

[1] This requirement has been dropped since 1882.

and the condition that creosote oil should be free from it seems quite uncalled for. This is also generally recognised in America, where, according to Tayne (*J. Amer. Chem. Soc.*, xxii. (1900), p. 614), the specifications now directly require 40 to 50 per cent. naphthalene to be present.

The different *requirements concerning the quality of the oil* made by some English and foreign creosoting-works are given on p. 549.

The table[1] given below shows the general character of different descriptions of creosote oils. The samples under A were the whole runnings of heavy oils distilled from samples of tar obtained from twenty different Metropolitan gas-works. The samples under B were produced at the Beckton tar-works, and represent oils from which portions of the green oils and naphthalene were excluded; they are hence rich in tar-acids and rather less volatile than A. The liquefying-point of the B samples ranged from 36°·7 to 32°·8 C., and the point of turbidity on cooling from 31°·1 to 28°·3. The samples in series C are country creosotes, analysed by L. Archbutt. All were completely fluid at 32°, and many at 15°·6. The sample yielding 72 per cent. of distillate and 13·5 of tar-acids was the product of special treatment. The samples in series C are probably somewhat richer in tar-acids than the generality of country oils:—

	Spec. grav. at 82° C.	Percentage of distillate below 315° C.	Percentage of tar-acids from distillate.
A. Heavy London oils: highest .	1·075	79	8·0
„ „ „ lowest .	1·048	60	3·0
Average of 20 samples . .	1·0588	71·5	5·6
B. Partial runnings from London oils: highest	...	91	10·2
Do. lowest . . .	...	78	8·2
Average of 20 samples . .	...	82·8	9·15
C. English country oils: highest .	1·056	90 „	24·0
„ „ „ lowest .	1·024	72	13·5
Average of 18 samples . .	1·0335	81·8	18·6

The creosote oils distilled in London and from tar made of Newcastle coal are generally richest in naphthalene and high-boiling constituents, and contain but a moderate percentage of

[1] From Allen's *Comm. Organ. Anal.*, 2nd edition, vol. ii., p. 555.

tar-acids. "Country oils," or oils from the Midland district, are lighter, thinner, and more volatile than "London oils"; they usually contain less naphthalene and more tar-acids. Scotch oils, which are largely derived from cannel coal, are still thinner and more volatile, and sometimes lighter than water.

The present state of the important question as to what is the best quality of coal-tar oil for creosoting purposes is very clearly elucidated, for which I am indebted to the kindness of Mr S. B. Boulton, and which is printed *in extenso* in the former editions of this treatise. In this edition we will only quote its salient points.

Liebig's theory of the destruction of organic substances by "eremacausis" is now antiquated, and so is the idea that putrefaction can be avoided by coagulating the albumen. The germ theory is now universally adopted, and we may take it for certain that antiseptics must either kill the germs, or prevent them from entering the substance, or both. The choice of antiseptics must be regulated by circumstances. For hygienic and therapeutic purposes the volatility and solubility of the antiseptics are frequently even of advantage, but for timber exposed to the atmosphere and to moisture it is otherwise. Here those antiseptics are more permanently successful which resist moisture and fill up the pores of the wood with substances inimical to the development of destructive organisms. Here, again, volatile oils, as petroleum, etc., have necessarily failed and the creosote oils have proved to be the most successful. From 1838 to 1860 they were applied without much chemical research having been made about them. When the value of carbolic acid began to be recognised, it was considered the most potent agent in this case as well, but later on it was found that it is not so, carbolic acid (C_6H_5OH) being too volatile and soluble in water. The higher phenols contained in the heavier and later distillates, are far superior for our purpose to carbolic and cresylic acid. Naphthalene is now also known to be a most useful antiseptic, and since all properly conducted creosoting operations are now carried on at a temperature of at least 50° C., it can be injected without the slightest difficulty.

Its after-consolidation within the pores of the wood is very useful, as it tends to resist the exudation of the more fluid oils, and the incursion of water and micro-organisms. Practical

experiments, extending over a number of years, have shown that the carbolic acid, contained in creosote, disappears within twelve months, whereas wood treated with the heavier oils used for railway-sleepers, fences, etc., has been found perfectly sound by different investigators even thirty-two years after its being put into place. This timber contains no carbolic acid, but the heavier and less volatile oils, most of them not distilling under 300° C.; also acridine and cryptidines, and mostly naphthalene, sometimes in considerable quantities.

These opinions of Mr Boulton to a great extent coincide with those expressed in a report by Dr C. Meymott Tidy, made to the directors of the Gas-Light and Coke Company in 1883, and printed in our former editions. He does, however, attribute more importance than Mr Boulton to the coagulation of the sap albumen, brought about by the tar-acids. Otherwise these acids have but little value for preserving sleepers, etc., as they seem to be entirely dissipated within a very short time. The naphthalene does very great service, and so do the heavy oils distilling not under 600° F. (316° C.). This investigation led Dr Tidy to draw up a specification which follows here in the form given to it in 1885.

"*Dr Tidy's Specification for Creosote* (*as amended in* 1885).

"1. That the creosote shall be completely liquid at a temperature of 100 F. [38° C.], no deposit afterwards taking place until the oil registers a temperature of 95° F. [35° C.].

"2. That the creosote shall contain at least 25 per cent. of constituents that do not distil over at a temperature of 600° F. [316° C.].

"3. That, tested by the process hereafter to be described, the creosote shall yield a total of 8 per cent. of tar-acids.

"4. That it shall contain no admixture of bone oil, shale oil, or of any substance not obtained from the distillation of coal-tar; and that the first 25 per cent. of the distillate shall have a specific gravity greater than that of water.

"*Process to be adopted for determining the Coal-tar Acids.*

"1. One hundred c.c. of the well-mixed creosote is to be distilled at a temperature of 600° F. until no further distillate

comes over. The distillate so obtained is to be mixed and well shaken in a stoppered flask with 30 c.c. of a solution of caustic soda, of sp. gr. 1200. The mixture is then to be heated. This done, the stopper is be replaced in the flask, and the hot mixture again shaken vigorously for at least a minute.

"The contents of the flask are now to be poured into a separating-funnel (Fig. 151), and the soda solution drawn off. The creosote is to be heated a second and a third time in a similar manner with the caustic-soda solution, except that only 20 c.c. of the soda solution shall be used for the second and third extractions, instead of 30 c.c., as in the first extraction.

"2. The three soda solutions are now to be mixed together. *When cold*, any particles of creosote are to be got rid of by means of a separating-funnel. This done, the solution is to be thoroughly boiled, in order to expel the last traces of creosote present in the solution. The mixture is then to be allowed to cool. When cold, dilute sulphuric acid (1 of acid to 3 of water) is to be added (about 35 c.c. will be required) until the solution becomes slightly acid to litmus. The whole is then to be poured into a separating-funnel, and allowed to stand until perfectly cold, and the tar-acids well separated.

FIG. 151.

"3. The tar-acids are now to be dissolved in 20 c.c. of the caustic-soda solution (sp. gr. 1200) and 10 c.c. of water. The mixture is then to be boiled and filtered through a funnel fitted with a plug of asbestos. The asbestos plug is to be washed with not more than 5 c.c. of boiling water. The solution is to be allowed to cool *perfectly* in a 100 c.c. measure. It is then to be rendered slightly acid with dilute sulphuric acid (1 to 3) (10 c.c. will probably be found sufficient for this purpose). The whole is again allowed to stand *for two hours* until *perfectly cold*, when the percentage of the tar-acids is to be read off.

"*Process to be adopted in estimating the quantity of Distillate.*

"The operation is to be conducted in a retort (fitted with a thermometer), and heated with the naked flame of a Bunsen burner. The heat applied is to be gradually raised to 600° F.,

and continued at that temperature until no further matters distil over. The distillation of the 100 c.c. should be completed within half an hour."

The above has been entirely upheld by a new report, made by Dr Tidy to the Gas-Light and Coke Company on 11th February 1885, in reply to a paper by Dr Voelcker and to the specification suggested by that gentleman. We now append the reasons given by Dr Tidy for some of the above details:—

"1. The omission of any clause specifying the specific gravity of the creosote to be used. I have done this advisedly, because of the extreme difficulty in taking the gravity of creosote at normal temperatures with the 1000-grain bottle, and the practical uselessness in my judgment of employing a hydrometer for the purpose. If it be considered necessary to introduce a specific-gravity clause, I would suggest that the gravity be between 1040 and 1065, water being 1000. I am of opinion, however, that for practical purposes a specific-gravity clause is altogether unnecessary.

"2. Believing strongly as I do in the value of those constituents of the oil that are the most difficult to volatilize, I have deemed it right to suggest a clause to the effect that the creosote shall contain at least 25 per cent. of matters that distil over above 600° F.

"3. I have made a large number of experiments as to the best method by which the estimation of the tar-acids may be determined.

"I note—

"(*a*) That very slight differences in the strength of the solutions used, and in methods of manipulation, considerably influence the results obtained. I therefore deem it necessary that, as a part of the specification, the process to be employed for estimating the acids should be exactly stated.

"(*b*) I have failed to discover any easy method of separating the carbolic from the other tar-acids. I have tried for this purpose numerous experiments, but with such unsatisfactory results that I have decided to recommend that the total quantity of tar-acids only should be stated. Further, the fact that as preservatives one kind of tar-acid is, so far as we know, as good as any other, renders a further separation of the acids in my

judgment unnecessary. My analyses of samples will show that in fixing not less than 8 per cent. of total tar-acids, we obtain a fair index of the purity and genuineness of the creosote."

We now give

Sir F. Abel's Specification, 2nd January 1884, *for Creosote.*

"The creosoting liquor is to be of the description known as heavy oil of tar obtained by the distillation of coal-tar, and consisting of that portion of the distillate which comes over between the temperature of about 350° F. (176° C.) and that of 760° F. (405° C.).

"The liquor must be free from admixture with any oil or other substance not obtainable from such distillate. It shall contain not less than 20 nor more than 30 per cent. of constituents that do not distil over at a temperature approaching 600° F. (316° C.).

"It must yield not less than 9 per cent. by volume of tar-acids when tested in accordance with the instructions annexed.

"The creosoting liquor must become completely fluid when raised to a temperature of 100° F. (38° C.), and exhibit no signs of any deposit on cooling down to a temperature of 90° F. (32½° C.).

"The specific gravity of the liquor must not be less than 1·035, and not more than 1·065 at a temperature of 90 F., as compared with water at 60° F.

"*Test for Creosoting Liquor.*

"1st. The liquor, if necessary, is to be warmed until it is perfectly fluid.

"A. One hundred c.c. is then to be placed in a glass retort of convenient size, and subjected to distillation until a temperature of nearly 600° F. is attained.

"The thermometer regulating the temperature must be so placed in the retort that at the commencement of the distillation the bulb of the thermometer is entirely immersed in the liquid, but not touching the bottom of the retort. The distillate should be collected in a stoppered-glass bottle, having a capacity of about 200 c.c.

"2nd. The distillate is to be mixed with 20 c.c. of a solution

of caustic soda (sp. gr. 1·21), the mixture being shaken at intervals for a period of not less than three hours, and is then to be transferred to a burette provided with a glass tap, into which has previously been introduced a few drops of soda solution sufficient to fill the narrow space above the stopcock. The burette, with its contents, is then to be set aside for twelve hours, in a place sufficiently warm to keep the liquid fluid. The soda solution containing the tar-acids will then be found to have separated from the other portions of the creosoting liquor, occupying the lower portion of the burette, and should then be drawn off into a small glass flask, which should have a capacity of about 100 c.c., and be provided with a long narrow neck (divided into cubic centimetres) of sufficient length to be capable of holding the whole of the tar-acids afterwards separated. The liquor not acted upon by the soda solution is to be returned to the bottle by inverting the burette. Ten c.c. of fresh soda solution is then to be added, and the mixture again treated as before. The soda solution from this second treatment, containing any further amount of tar-acids not extracted by the first treatment, is then to be added to the soda solution first obtained in the long-neck flask. Sulphuric acid, dilute (1 vol. of oil of vitriol and 3 vols. of water), is now to be gradually introduced into the flask until a very slightly acid reaction is produced, the flask being kept cool. Then enough mercury is poured into the flask to drive all the tar-acids up into its neck, where their volume can be read off on the graduation.

"*Note.*—If the creosoting liquor is of an unusually thick consistency, it may be found necessary to subject it to a preliminary distillation, which should be conducted as described at A; but the use of a thermometer is not necessary, as the distillation should be continued until nothing further comes over."

It will be seen that Abel's specification very nearly agrees with Tidy's, and that the separation of carbolic and cresylic acid by fractional distillation of the tar-acids, formerly prescribed by Sir F. Abel, but objected to by me in the first edition of this treatise (p. 208) as quite illusory, has been dropped. Tidy's prescription of boiling the alkaline solution of the tar-acids, in order to expel any hydrocarbons, is, I think, quite called for; but then Abel requires 9 per cent. in lieu of 8 per cent., which

will compensate for the impurities left by his treatment in the tar-acids.

The *tests made at the works* are mostly more simple than the above. The *density* is best ascertained at about 32°, when the oils are all fluid, by means of a hydrometer, or else by a specific-gravity bottle, which is allowed to cool down to 15°, when the stopper is pressed in tightly. The *liquefying-point* is found by placing some of the oil in a test-tube, inserting a thermometer and moving about in a warm-water bath; the *point of turbidity*, by allowing the whole to cool down. The *distillate up to* 315° is found by heating 100 c.c. in a 4-oz. retort by a small naked flame, protected by a tin cylinder. The thermometer ought just to touch the liquid remaining at the end. The distillation should last about thirty minutes. The *tar-acids* are usually estimated in the distillate by treating it twice with 30 and 15 c.c. of caustic-soda solution of sp. gr. 1·21, at a gentle heat, separating the oil by a tap-funnel, cooling down, adding 30 c.c. of dilute sulphuric acid (1 acid to 3 water, transferring to a graduated cylinder), allowing to *cool completely*, and reading off the volume of tar-acids separated (Messrs Burt, Boulton, & Haywood).

If the *basic constituents* are to be estimated, the rules mentioned in Chapter X. must be observed.

The American Railway Engineering Association, in its *Bulletin*, No. 65, of July 1905, gives "Standard methods for analysis of coal-tar creosote," the main feature of which is distillation in the old English retort apparatus, long ago recognised as being most unreliable for fractionations.

A recent (1904) specification of the Prussian Railroad Management for impregnating oils contains the following conditions:—"The tar oils must be composed in such manner that on distilling them (the thermometer being kept in the vapour) up to 150° C. at most 3 per cent., from 150° to 255° at most 30 per cent., and from 150° to 355° at least 85 per cent., pass over. The specific gravity at 15° is to be between 1·04 and 1·10. At this temperature the oil should be perfectly clear, and show no secretion of solid naphthalene when a few drops are poured upon a layer of filtering paper. Its percentage of phenolic substances, *i.e.*, such as are dissolved by caustic-soda solution of sp. gr. 1·15 at 15°, should be at least 10 per cent."

To this Kraemer and Spilker remark that these conditions are fulfilled by a mixture of equal parts of creosote oil and filtered anthracene oil, but that they cannot be fulfilled by oils containing more than 20 per cent. phenols, unless the former method (keeping the bulb of the thermometer within the liquid) be admitted.

The testing for phenols is done by shaking 100 c.c. oil with 100 c.c. caustic-soda liquor of sp. gr. 1·15 at 15° C. in a graduated 200 c.c. cylinder, allowing to stand for three or four hours, and observing the reduction of the volume of the oil, which is taken as indicating the percentage of phenols.

Instead of employing creosote oil by itself, it has become very usual to combine with it the action of other antiseptic agents, in the first place *chloride of zinc*, which for a long time has been employed by itself for the pickling of timber (*cf. supra*, p. 540). This has been done for many years at the various factories owned by the Rütgers Company. A special form of such a combination is that patented by Guissani (Ger. P. 132202), who first removes the moisture from the wood by keeping it in a vacuum in a high-boiling liquid, and then dips it in an open vessel in creosote oil of sp. gr. 1·09, overlaid by an aqueous solution of zinc chloride of sp. gr. 1·02. Emulsions of creosote oil with solutions of zinc chloride are described by the Berliner Holzkomptoir (Ger. Ps. 139441 and 152179; *supra*, p. 528).

Nördlinger-Flürsheim (Ger. Ps. 121904 and 168611) increases the antiseptic action of tar oils by adding to them the neutral or acid metallic salts of propionic acid and its homologues up to caprinde acid, or of the acids of the acrylic series. These are soluble in the tar oils, and not easily removable by water.

Decomposition of Heavy Tar Oils by Heat (*cracking*).

This is sometimes done in order to utilize otherwise comparatively valueless oils or oily residues by exposing them to a high degree of heat—*e.g.*, passing them through red-hot tubes ("cracking"). Usually the main object was that of making illuminating-gas; but with this was associated the getting of more valuable oils. We have seen above (p. 144) that both benzol and anthracene can be obtained in this way from the heavy residues of petroleum, browncoal-tar, and wood-tar. Many

chemists have worked in this direction, as Breitenlohner,[1] Vohl[2] (who believes this process to be practicable), Walker and Smith,[3] and others. [Kraemer (priv. comm.) declares the hydrocarbons of coal-tar to be much less suitable for the "cracking process" than the paraffins, especially petroleum distillates; the former yield but a small quantity of benzol, etc., or of illuminating bodies in general.] An apparatus specially constructed for the purpose in question was patented in 1861 by the Paris Gas Company;[4] it is represented in Fig. 152. It consists of a set of cast-iron cylindrical retorts, *a*, closed at one end and provided at the other end with a movable cover. About 12 inches from one end there is a partition, *b*, 8 or 12 inches high, which prevents the oil from running towards the part not exposed to the fire. The space thus shut off communicates by an ascending pipe, *c*, with a receiver, *d*, which is connected by *e* with another receiver, *d'*, both alike intended for heavy products of condensation: these are removed by the pipes *g g'*; whilst the vapours not yet condensed pass through the worm *f* and are collected in *h*. *l* carries away the incondensable gases. The heavy oil runs from the tank *k* through a tap, *j*, into the funnel *i*, and thence in a continuous stream into the retort *a*, previously brought to a red-heat. There the oil spreads as far as the partition *b*, and is decomposed into graphite (remaining in the retort) and volatile products (passing over the partition and through the pipes into the receivers). In *d* and *d'* a heavy, tarry liquid condenses; it is mixed with more heavy oil, and again run back into the retort [nowadays it would probably first be worked for anthracene]. The liquid condensed by the worm *f*, and collected in *h*, is rich in benzol, and is treated like ordinary crude naphtha. The gas escaping at *l* is employed for lighting, and was considered the principal product.

Behrens[5] employed for a similar purpose a retort made of firebricks, heated from below. It was heated up to a very bright red-heat; and a continuous jet of heavy oil was run into it by a swan-neck pipe. The volatile products were condensed

[1] *Dingl. polyt. J.*, clxvii., p. 378; clxxv., p. 392. [2] *Ibid.*, clxxvii., p. 58.
[3] *Wagner's Jahresber.*, 1867, p. 752.
[4] *Technologiste*, 1861, p. 145; Girard & Delaire, *Dérivés de la Houille*, p. 20.
[5] *Dingl. polyt. J.*, ccviii., p. 361.

by an ordinary hydraulic main and by very wide pipes, which nevertheless were frequently choked up with naphthalene and soot. In the hydraulic main (at the base of the furnace) most

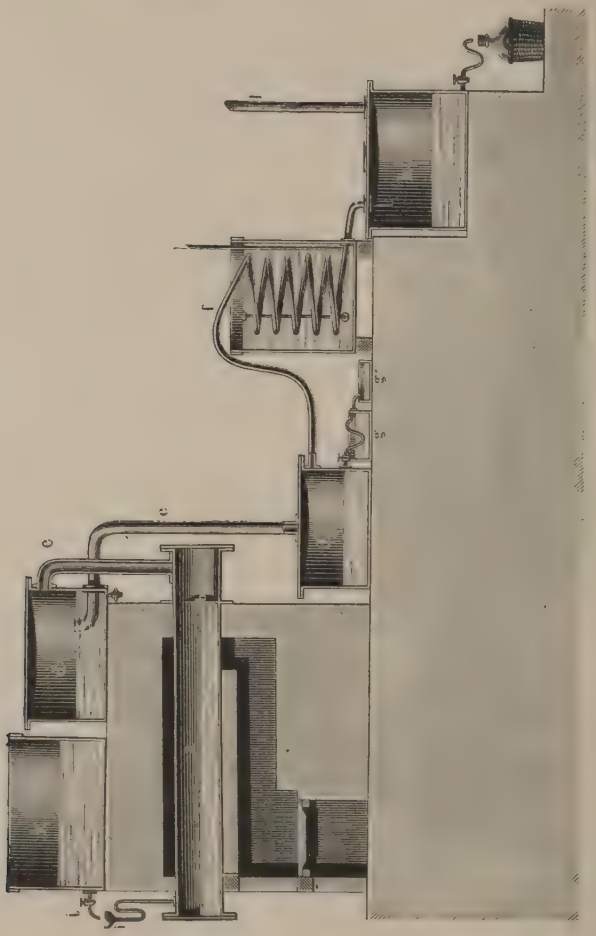


FIG. 152.

of the undecomposed oil was condensed; the remainder together with naphthalene and the more volatile hydrocarbons newly formed, condensed in the cooling-pipes. In this way the

heavy oil yielded on an average 2 per cent. benzene and toluene, and a little xylene and higher homologues. Below and above the temperature just mentioned, less of the more volatile hydrocarbons was formed. In the former case but little heavy oil was decomposed;[1] in the latter the benzene was converted into naphthalene. In the furthest part of the condensing-apparatus, naphthalene, benzene, and toluene were collected. The graphite remaining on the furnace-bed could be obtained in large pieces, and was valuable for producing high temperatures.

Of course the apparatus employed at Nobel's works, at Baku, for decomposing petroleum residues (p. 145), could also be used for creosote oil.

G. E. Davis's proposal to convert all the distillates from tar, except naphthalene and anthracene, into gas, as described pp. 405 *et seq.*, may be mentioned in this connection.

Kenyon (B. P. No. 13627, of 1887) passes steam and heated vapours of tar oil, with a little air, into two retorts filled with coal, conducting the gases from the retorts charged later on into that charged at first. If it is intended to increase the yield of ammonia and aromatic hydrocarbons, the retorts are charged with coal rich in H, O, and N, together with waste leather, hair, etc. The escaping vapours are freed from anthracene and aromatic hydrocarbons by washing with heavy oils, cooled down to the freezing-point. (*Cf.* Kraemer's opinion on the Dinsmore process, p. 250.)

Formerly it would rarely have paid to convert tar oils into gas; at present the price of creosote oil would be no obstacle to this process, but it is very doubtful whether there is any advantage in it (*cf.* L. T. Wright, p. 407).

According to J. Young, heavy paraffin oils can be converted into light ones by heating them in strong iron boilers under a pressure of 1½ atmospheres. Possibly this would apply also to heavy coal-tar oils; but evidently nothing can be said as to the probable cost, yield, and so forth.

Boleg (*cf.* p. 529) studied more closely the distillation of creosote oil under pressure. When employing 3 or 4 atmospheres' pressure and purifying with sulphuric acid and caustic-soda solution, a lighter, thinner, orange-coloured oil, almost

[1] Hence the cast-iron retorts patented by the Paris Gas Company (p. 559) cannot have stood a very long time, as they would have to be heated too high.

devoid of smell, was obtained, which might be used in the same way as "carbolineum" (p. 483), even for inside work. The naphthalene contained in the crude oil was also easily obtained, but no lighter oils.

G. Schultz (Ger. Ps. 101863 and 105582) introduces creosote and anthracene oil into the gas-retorts and coke-ovens during the distilling process, thus converting those oils into more valuable hydrocarbons, such as benzol (*cf.* pp. 144 *et seq.*).

On p. 292 we have already mentioned Wirkner's process (B. P. 13185, of 1903; Ger. P. 158731) who converts tar "or tar oils" into pitch by heating with sulphuric acid, and the process of the Chem. Fabr. Flörsheim Dr Nördlinger, which consists in heating tar or tar oils to 120° to 150° C. in the presence of air, oxygen or ozonized air, until the derived product has been obtained.

A great many patents have been taken out for decomposing heavy tar oils by heat so as to render them, or the products obtained therefrom, available for driving motors of all kinds (*cf. supra*, p. 531).

Application of Creosote Oil for the "Blue-steaming" of Bricks.

The ancient Romans, as is shown by ash-urns, etc., understood the process of imparting to earthenware a fine slate-grey colour. They effected this by putting green wood into the brick-kilns, after finishing the burning process proper, and keeping the kilns closed; and this process is in use at the present day in Holland, where alder-wood is employed for the purpose. These Dutch "blue-steamed" bricks are extensively employed on account of their pleasing colour and their resistance to the weather.

In Germany the agent universally used for this purpose is creosote oil freed from naphthalene by keeping through the winter season. When the bricks have been sufficiently burnt, all openings in the kiln are closed with clay or sand and the damper let down. The oil is then run in through cast-iron pipes passing through the brickwork, in small portions at a time. The oil is at once vaporized and decomposed, carbon in the graphitic state being deposited on the surface and in the pores of the bricks and staining these grey with metallic lustre.

When enough oil has been run in (as known by experience), water is run through the same pipes in several portions; this cools the bricks, so that the carbon is not burned on contact with air, and the quicker the cooling, the finer the colour.

This process must be carried out in periodically working, very strongly built kilns. Ch. and I. Lengsholz (Ger. P. 95882) describe a special kiln for this purpose. Ludowici (*Tonindustrie Zeitung*, 1898, p. 38) shows that porous material is better than dense bricks, as is easily understood. The iron salts must also be reduced to protoxide, which greatly influences the colour. One thousand bricks require on the average 20 kg. of blue-steaming oil, but this depends on the percentage of iron. The opinion of Hoffmann (*ibid.*, 1898, p. 38), that in this process a kind of asphalt is formed, is not very conclusive, considering the high temperature.

The filling up of the pores with graphite would easily explain the greater resistance to the rain and frost, claimed for these bricks.

Carriage of Creosote Oil.

On a comparatively small scale creosote oil is conveyed in wooden casks, which are very liable to leak unless they have been previously saturated with a solution of glue. On a larger scale exactly the same contrivances are employed as for tar itself, viz.:—for railway carriage, block waggons with cylindrical or angular wrought-iron tanks holding 10 or 15 tons; for water carriage (on rivers or canals), tank-boats.

END OF PART I.

BIRMINGHAM REFERENCE LIBRARY

PRINTED BY
OLIVER AND BOYD
EDINBURGH